Separation Parameters using Ionic Liquid Mixtures: Analysis by Inverse Gas Chromatography Measurements

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Dissertation presented by the double degree program between Federal Technological University of Paraná and Polytechnic Institute of Bragança

Escola Superior de Tecnologia e Gestão

Instituto Politécnico de Bragança

for the double degree program with

Universidade Tecnológica Federal do Paraná

In order to obtain a master's degree in

Chemical Engineering

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Bragança
June 2021

"Our greatest weakness lies in giving up. The most certain way to succeed is always to try just one more time."

Thomas Edison

Acknowledgments

Abstract

This work discusses the potential of imidazolium-based ionic liquids as potential in the fractionation of terpene mixtures, also giving information relevant to study other separation processes such as the desulfurization and denitrification of fuel oils. Besides pure [C$_{12}$mim]Cl, the equimolar mixture [C$_4$mim][C$_{12}$mim]Cl of ionic liquids was also tested. The separation capacity between solutes and ionic liquids can be calculated from infinite dilution activity coefficients, measured experimentally for 40 solutes; water, common organic solvents and terpenes in both ionic liquids using inverse gas chromatography, in the temperature range of 333.15 to 423.15 K.

The values for the activity coefficients at infinite dilution are very small for terpenes and terpenoids, indicating a strong interaction, possibly due to the high basicity of the anion and the high apolarity of the cation. Selectivities were obtained for hypothetical binary mixtures containing α-pinene oxide but showing, in general, low capacities. However, preliminary results showed that the combination of two ionic liquids could present better selectivity values than pure ionic liquids, which is an open area to be explored.

Keywords: ionic liquids, terpenes, terpenoids, separation, activity coefficients at infinite dilution.

Resumo

Este trabalho discute o potencial dos líquidos iônicos à base de imidazólio como potenciais agentes de separação no fracionamento de misturas de terpenos, também fornecendo informações relevantes para o estudo de outros processos de separação, como a dessulfurização e desnitrificação de óleos combustíveis. Além do $[C_{12}mim]Cl$ puro, a mistura equimolar $[C_4mim][C_{12}mim]Cl$ de líquidos iônicos foi também testada. A capacidade de separação entre solutos e líquidos iônicos pode ser calculada a partir de coeficientes de atividade de diluição infinitos, medidos experimentalmente para 40 solutos; água, solventes orgânicos comuns e terpenos em ambos os líquidos iônicos usando cromatografia gasosa inversa, na faixa de temperatura de 333,15 a 423,15 K.

Os valores dos coeficientes de atividade a diluição infinita mostraram-se muito baixos para terpenos e terpenóides, indicando uma forte interação desses com os líquidos iônicos, possivelmente devido à alta basicidade do ânion e à alta apolaridade do cátion. Seletividades foram obtidas para misturas binárias hipotéticas contendo óxido de α-pineno, mas associadas, em geral, com baixa capacidade. No entanto, resultados preliminares mostraram que a combinação de dois líquidos iônicos poderá apresentar melhores valores de seletividade do que líquidos iônicos puros, que é uma área de investigação a ser explorada.

Palavras-Chave: líquidos iônicos, terpenos, terpenoides, separação, coeficiente de atividade a diluição infinita.

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List of symbols and acronyms

List of Symbols

P_i	column inlet pressure
P_o	column outlet pressure
U_0	column outlet volumetric flow rate
B_{ab}	crossed second virial coefficient
$\bar{H}_m^{E,\infty}$	excess enthalpy at infinite dilution
$\bar{S}_m^{E,\infty}$	excess entropy at infinite dilution
$\bar{G}_m^{E,\infty}$	excess Gibbs free energy at infinite dilution
V_a^*	molar volume of pure compound a
V_N	net retention volume
n_a	number of moles of compound a
V_a^∞	partial molar volume of pure compound a at infinite dilution
J_2^3	pressure correction term
t_a	retention time of compound a
B_{aa}	second virial coefficient of pure compound a
T	temperature inside oven of the gas-chromatographer
P_a^*	vapor pressure of pure compound a
S_{ij}^∞	selectivity
k_j^∞	capacity

Greek Letters

γ_{ab}^∞	activity coefficient at infinite dilution of compound b in LI

List of Acronyms

COSMO-RS   conductor-like screening model for real solvents

DES	deep eutectic solvents
GC	gas chromatography
GRAS	generally recognized as safe
GLC	gas-liquid chromatography
HBA	hydrogen bond acceptors
HBD	hydrogen bond donors
IDAC	infinite dilution activity coefficient
IL	ionic liquid
LVE	liquid-vapor equilibria
NRTL	non-random two-liquid model
TCD	thermal conductivity detector
UNIQUAC	universal quasichemical

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Chapter 1. Introduction

1.1 General Context

With a growing worldwide demand for environmentally friendly and sustainable products, without neglecting quality, driving research, development, and innovations to the use of natural products with applications in the industry is an evident trend. In this way, essential oils and plant matrices are in a prominent position, being one of the most relevant classes of biomass for industrial applications.

With great relevance, essential oils (EO) are raw materials of great importance for the pharmaceutical, food, cosmetics, flavoring, and beverage production industries. Due to this great use of essential oils, in the year 2018, the exports reached the value of US $ 6.22 billions, having an increase of 12.5% in the exports compared with 2017, being the main exporters India (13.2%), United States (12.6%), France (8.26%), and Brazil (7.13%). [1] Among the essential oils, one of the most used is the citrus essential oil, the main product in 2015, reaching 30% of the market. Orange essential oils consist of about 95% by weight of terpenes, mainly limonene 5% by weight of terpenoids, mainly linalool, and less than 1% by weight of volatile compounds. [2]

1.2 Terpenes and Terpenoids

Terpenes and terpenoids are the main compounds of essential oils, terpenes are unsaturated hydrocarbons, and can be oxidized, contributing to the formation of unpleasant flavors, making their application and commercialization difficult. [2] Even though terpenes are the main compound, they have little influence on the aroma and flavor of essential oils because they can undergo hydrolysis reactions with the influence of light, heat, and air. [3] On the other hand, oxygenated derivatives are known as terpenoids (4) and have better organoleptic properties, greater stability, and higher solubility in polar media. (3) Even with high demand, they are present in low concentrations, so they tend to be expensive or even unfeasible to be exploited. (4) Seeking to

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improve and make production more profitable, ways were sought to separate terpenes and terpenoids, reducing unpleasant odors and improving product quality and stability. (5)

1.3 Methods of Separation

The process of separating essential oils is usually called deterpenation, this process is used to separate the fractions of the oxygen-rich terpenes from the non-oxygenated terpenes. The fraction with a high concentration of oxygenated compounds with alcohols, esters, aldehydes, ketones, and carboxylic acids are responsible for the organoleptic properties and fragrances, on the other hand, the hydrocarbon terpenes are mostly monoterpenes, and sesquiterpenes and their contribution to the aroma is minimal, being also poorly soluble in water and are easily oxidized. (6)

The separation process of the essential oils commonly found are solvent extraction, distillation, and membrane or supercritical methods. The solvent extraction technique uses thermodynamic concepts and is based on the difference in solubility of the target compound in the two immiscible liquid phases. (7) Distillation uses the relative volatility of compounds over a range of temperatures to perform the separation. (7) Membrane separation is interesting for replacing solvent extraction as it presents greater purity in the selective separation of oxygenated terpenes. (7), (8) Fractionation using supercritical fluids is based on the solvation properties of the supercritical fluid, so it is possible to use pressure and temperature above the critical point of the compound, mixture, or element. (7)

Seeking to improve the separation process between terpenes and terpenoids, reducing environmental and harmful impacts, another class of compounds has emerged with great properties with the potential to replace organic solvents. (6) Ionic Liquids (IL) are salts with a melting point below 100 °C. They are usually formed by large organic cations and smaller anions and can be designed by modifying their anions or cations. (9) IL also has interesting properties such as low vapor pressure, thermal stability, and is non-flammability, being considered green entertainers in the separation of essential oils. (10,11)

The design of ionic liquids has evolved in level due to the possibility of adjusting chemical and physical properties or mixing ionic liquids to achieve the desired properties. (12) Some studies have also shown that mixtures of ionic liquids are interesting due to the possibility of design properties combining ionic liquids, so it is possible to select ionic liquids for the mixture of IL and also cations and anions for the formation of ionic liquids, which are both possible ways to design the best solution for a given separation process. (12)

Another class of solvents is growing exponentially, showing promising features for application in the separation process. Deep Eutectic Solvents (DES) are seen as green solvents, and as an alternative to conventional organic solvents and ionic liquids. They are mixtures of two or more compounds that, when combined, decrease the melting point, well below the initial melting point of the pure compounds. (13) The outstanding properties of these solvents are the very low vapor pressure, wide liquid range, tuneability, high thermal stability, solvency capacity, and non-flammability. (2)

1.4 Infinite Dilution Activity Coefficient

The data necessary to use in the selection process of traditional separation agents such as distillation or solvent extraction can be obtained in two ways through the phase diagram or infinite dilution activity coefficient. Using the phase diagrams in terms of temperature, pressure, and composition, but this method is time-consuming, the other way that can predict the properties of the separation agents is the activity coefficients at infinite dilution, this method indicates the interactions between the solvent and solute and is an important parameter for estimating selectivity and capacity and can thus be used to estimate the performance of the separation. (14–16)

1.5 Objective

Due to the growing demand for essential oils, mainly citrus fruits, which are made up of terpenes and terpenoids, it is necessary to find efficient separation methods. A popular separation method in the industry is distillation, however for thermosensitive compounds, it is not possible to apply this method that normally uses high temperatures, so it is necessary to study separation

agents that facilitate the separation and purification of the compounds, maintaining their properties and without increasing installation and operating costs.

Ionic liquids and deep eutectic solvents appear in this context of improving the separation and purification processes as possible more efficient separation agents. Due to the number of different possibilities, a simpler and more efficient way to study separation agents and select them for specific purposes is to measure the activity coefficients in infinite dilution, which allows estimating the separation properties with selectivity and capacity that can guide the proper selection of the best separating agent.

Chapter 2. State of the Art

2.1 Compounds

2.1.1 Essential Oils

Essential oils are complex mixtures of aromatic hydrocarbons consisting of terpenes, terpenoids, and some other volatile compounds, synthesized by living organisms and are obtained as sub-product processing of fruits and plants. (17)

Essential oils are unstable and so easily the quality of their characteristics decreases, as well as their commercial value. (18) According to Gonçalves (2018) limonene is the main terpene in citrus essential oils with a highly varied composition of the oxygenated fraction. Due to this great variety of components, the industrial fractionation of citrus essential oils is carried out by vacuum distillation. Due to the proximity of the boiling point of the oxygenated compounds to those of the terpenes, this can generate problems in the separation process making the separation very expensive or even making it impossible. (5)

2.1.2 Terpenes

Terpenes and terpenoids are volatile compounds present in essential oils. They are mainly oxygenated hydrocarbons and some also contain nitrogen or sulfur derivatives. The mainly terpnes can be seen in the Figure 1, below. The compounds that contain oxygen in their structure are called terpenoids and can be found in the following functional groups of alcohols, esters, aldehydes, ketones, and carboxylic acids, while those without oxygen in their structure are called terpenes. (10,17) The " ene" suffix indicates the preference of double bonds in it is structure, or also known as an olefinic bond. (10)

Isoprene

Isoprenol

α-Pinene

Menthol

Guaiol
(Sesquiterpene)

Cembrene A
(Diterpene)
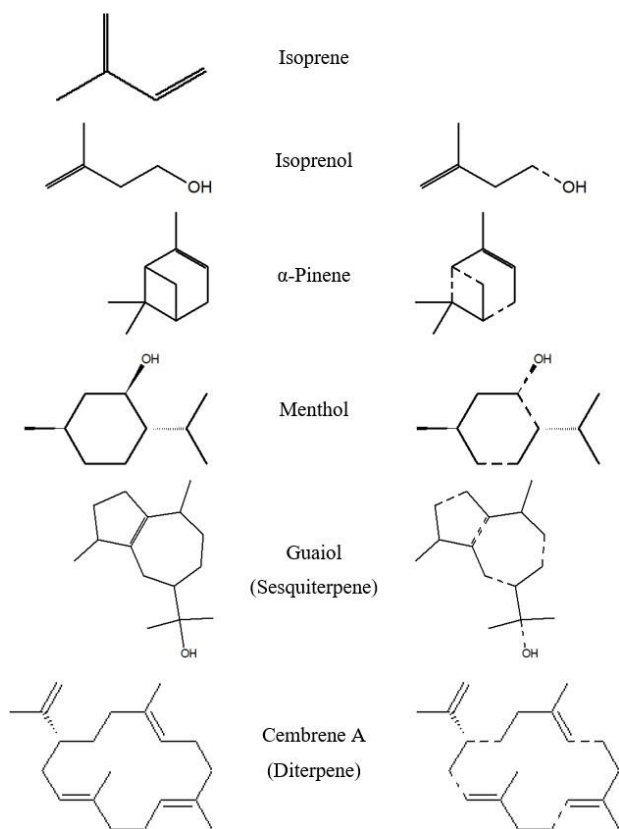
Figure 1 – Mainly terpenes structure.

Terpenes are built in blocks containing five carbons, the isoprene unit. Being connected to the "head" with the "tail" of the isoprene unit. (17) In this way, it is possible to from a wide range of structural variations for different applications. (19) Terpenoids are the most important components of essential oils, being also responsible for pleasant aromas and antioxidant properties, on the other hand, terpenes are easily oxidized, contribute little to fragrance, and also produce strange flavors, thus reducing the quality of essential oils. (15)

They are usually found in plants such as balms, cumin, cloves, citrus fruits, coniferous wood, coriander, eucalyptus, lavender, lemongrass, lilies, peppermint spices, rosemary, sage, thyme, and violet roses, are known for their aromas, flavors, and medical properties. (10) These compounds have complex and heterogeneous compositions, so they and up becoming more difficult to isolate their components. A large part of these compounds is generally recognized as safe (GRAS), (20) making them important for a variety of industrial applications.

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2.1.3 Ionic Liquids

Ionic liquids are revolutionary compounds, receiving great attention. (21) These new compounds are complex organic salt made up of long-chain organic cations combined with organic or inorganic anions. Unlike normal salts, ionic liquids can be in the liquid phase close to room temperature and pressure, with melting temperatures below 100 °C, due to it is the low density of ion charges with low symmetry, low volatility, good thermal stability, and solvatochromic capacity. (10,15) These properties make them interesting for use as an alternative solvent to traditional organic solvents for various chemical reactions and separation processes. (10,15) Categorized as "design solvents", ionic liquids have several possible combinations of cations and anions, which alter their thermophysical properties such as density, viscosity, heat capacity, thermal conductivity, and also their solvation capacity. In this way, ionic liquids provide a great number of possibilities of combinations to be applied. (15)

2.1.4 Deep Eutectics Solvents

Due to the search for new green solvents, a new class has been proposed. Deep eutectic solvents are a mixture of two or more compounds, formed by the complexation by hydrogen bonds, where the eutectic point is far below the melting point of each of the individual components. (10)

These new mixtures can be formed from the mixing of biodegradable and inexpensive materials, using mild temperatures, without chemical reactions, which means they can be classified as a green and safe solvent. A deep eutectic solvent depends on your starting materials to be renewable. DES can be classified as designed solvents due to the structural ability to combine hydrogen bond donors (HBD) and hydrogen bond acceptors (HBA), designing and adjusting their physical properties and phase behavior. (10)

Its characteristics such as low toxicity, non-volatility, non-flammability, and no reactivity with water and biodegradability are some of the properties that help them to be good solvents for different applications in catalysis, organic synthesis, dissolution processes, and electrochemical and chemical extraction of materials. (10) Being their physicochemical properties compared with

water and with ionic liquids of origin, they generally have greater specific mass and different melting points depending on the constituent materials.

2.2 Traditional separation methods

The process commonly known as "deterpenation", the separation of terpenes from terpenoids, is interesting to be used as a process to add value to terpenes. In this way it is possible to increase the purity, stability, and solubility of essential oils, thus making them viable to be used industrially. (2,22)

2.2.1 Solvent extraction

Liquid-liquid extraction is currently widely used in pharmaceutical and environmental sciences, being applied in the purification and separation of biological samples and/or concentration of samples with terpenes. (7,23)

The solvent separation process uses thermodynamic concepts and is based on the difference in solubility of the solute in the two immiscible phases. In practice, this extraction process takes place in two stages, the first the solute is dissolved in a solvent (S1), from which it is difficult to separate, and by contacting the solute is transferred to the other solvent (S2), from which it will be easier to separate. Finally, the solute extracted S2 undergoes a regeneration process, thus allowing reuse in a new extraction. (7,23)

To choose a suitable solvent to perform the separation, some physical properties must be previously evaluated, including its miscibility with water, proticity, volatility and toxicity, the solute distribution ratio, selectivity, and a comparison with other solvents in the literature. (7,24)

2.2.2 Distillation

The distillation process, unlike separation processes by chemical extraction, uses physical properties based on the relative volatility of chemical components at various temperatures. Essential oils are heat-sensitive compounds, so steam or vacuum distillation can be used to reduce

or prevent the degradation or transformation of the compound due to prolonged exposure to high temperatures. (7)

According to Nam et al., distillation can be categorized into two ways, fractional distillation at atmospheric pressure and steam distillation. (25) In order to improve the fractional distillation process and decrease the degradation of the essential oil, it is possible to decrease the boiling temperature of the crude essential oil, so that inside the column the degradation of the components is also less (26,27) for this case, the lower operating pressure also improves the relative volatility enabling a more efficient separation. (27) For steam distillation they are mainly used for the separation of chemical compounds sensitive to high temperatures, in this context the degradation of essential oils during the separation process can be avoided. (25)

2.2.3 Membrane separation

Membrane separation can be an interesting alternative for the separation of terpenoids from essential oils. (8) For liquid-liquid extraction, the interface between the phases are stabilized in a porous membrane. (8) During the separation process, the pores of the membrane are filled with one of two immiscible fluids, depending on the hydrophilic or hydrophobic nature of the membrane. [7] The membrane separation allows the use of a wide variety of solvents since the difference in density between the phases is not necessary as in the case of steps such as decantation. [8] The porous material usually does not interfere with the mass transfer selectivity, it is limited to putting the phases in contact without dispersion. [7]

Membrane separation has good advantages such as low energy consumption, facilitates product purification, and recovers valuable co-products from complex liquids, [27] however, it has some limitations, limited pressure range to ensure a stable interface between fluids, extra resistance to mass transfer, and relatively short membrane life. [28] For industrial applications, they are more severe, for example, the continuous decrease in the permeation flow, the polarization of the concentration, formation of gel layers, adsorption of surfactant molecules, and obstruction of the membrane pores. [29]

2.2.4 Supercritical Fluids

The extraction of volatile components has also been performed by supercritical fluids for many years to separate volatile compounds, essential oils, and phenolic compounds from plants on an industrial scale. [7,30] Supercritical fluids use physical-chemical properties with density, diffusivity, viscosity, and dielectric constant, thus enabling them to overcome the limitations of conventional extraction processes. [7,31] In this process, the solvation properties of the supercritical fluid are used, which can be achieved using pressures and temperatures above the critical point of a compound, mixture, or element. External factors such as the characteristics of the sample matrix and the interaction with the target analyte can also positively influence the separation. [7,32] Supercritical fluids allow adjustments of their properties before the separation process, making it possible to adjust the parameters for each separation making this class of agents more modellable than conventional methods. [32–34]

During this separation process, chemical solvents are not used, which makes it a green process with few environmental impacts. [32] The most used solvent in the separation by a supercritical fluid is carbon dioxide (CO_2) due to its important characteristics as it has no toxicity to human health, its critical temperature is close to the ambient temperature (31.2 °C) making it possible its use with bioactive and thermosensitive compounds and also for the ease of separating CO_2 from the oil reducing its pressure it returns to the gaseous state and can be reused. [31,35]

2.3 Alternative separation agents

2.3.1 Separation methods using ionic liquids

Currently, in the conventional separation processes in the industry, there is the accumulation of solvents due to the difficulty of recycling, this accumulation occurs because to reuse the solvents it is necessary to obtain the pure components. However, most of these mixtures are azeotropes, that is, it is not possible to perform the separation through traditional processes. The azeotropes are mixtures of two or more substances in a given composition that have a constant boiling point

as if they were a pure substance, and cannot be separated in the distillation process, for example. [36]

In order to separate these compounds, many methods have been proposed to separate azeotropes such as azeotropic distillation, extractive distillation, pressure oscillation distillation, liquid-liquid extraction, adsorption, and membranes. Of these processes mentioned above, extractive distillation is the most used process to separate azeotropes, but energy costs are high. In contrast, liquid-liquid extraction uses immiscibility between two phases at room temperature to make the separation process cheaper and more environmentally friendly. [36]

Ionic liquids have a great capacity for separating azeotropic mixtures, due to their low volatility at room temperature [37] and their ease of recycling has been considered as sustainable alternatives to conventional solvents. According to Pereiro et al. of the ionic liquids already studied, in approximately 75%, 1-alkyl-3-methylimidazolium was used as the cation, combining mainly with the anions of Cl^-, PF_6^-, BF_4^-, OTf^-, NTf_2^-, and $EtSO_4^-$. [36]

Generally, ionic liquids can be divided into imidazole, pyridine, tetraalkylammonium, tetraallyl phosphonium, among others. Of these ionic liquids mentioned above, the most common, stable and researched is imidazolium combined with chloride, bromide, hexafluorophosphate, tetrafluoroborate anions, neat or mixed with water or ethanol. [6,38]

Ionic liquids have aroused industrial interest due to the possibility to adjust their chemical and physical properties by choosing properly the right cation/anion combination, thus making it possible to design desirable properties and obtain more specific ionic liquids mixtures. [11]

Following the green chemistry principles, the mixture of two ionic liquids can be the right option for the development of new mixtures, discovering new properties and applications. [39] Research on these mixtures is growing rapidly and becoming popular due to their large number of applications. [11] The approach to the preparation of these mixtures must take into consideration:

i.   Some properties of ionic liquids can simply be predicted from an interpolation of the properties of the original constituents; [11]

ii.   Other properties are influenced by innumerable interactions that occur between ions, giving rise to the unique solvent property for the mixture that cannot be easily estimated from the properties of a pure ionic liquid. [11]

Considering the thermodynamics of the mixtures of ionic liquids, the first group is highly desired because the properties of binary mixture between ionic liquids provide properties of the mixture directly related to pure ionic liquids. The second group can provide mixtures with properties much different from the properties of pure constituents, suggesting an interesting perspective for the development of ionic liquids mixtures with new properties. The use of ionic liquids as solvent and binary, ternary mixtures requires further studies of their interactions, chemical and physical properties, and need to be understood more deeply. [11]

The work carried out by Ganem et al. studied the deterpenation of the mixture of essential oils, limonene, and linalool, through extractive distillation using the ionic liquid 1-butyl-3-methylimidazolium acetate as solvent. In this work, the liquid-vapor equilibria (LVE) in ternary systems were studied and modeled with the NRTL and UNIQUAC models. Through the simulation of the deterpenation of the citrus orange essential oil (limonene and linalool), they can be separated by extractive distillation using [C$_4$min][OAc] as entrainer. Operation is at low pressure (5 kPa) to avoid degradation of essential oil and ionic liquid. Using the unitary flash operation at 0.1 kPa and 423 K, maximum operating temperature obtained, practically pure limonene as a distillate and pure linalool as vapor from the flash unit, the entrained being fully recovered and returned to the process. [40]

2.3.2 Separation methods using deep eutectic solvents

Due to the search for new green solvents, a new class was proposed a few decades ago. Deep eutectic solvents (DES) are a mixture of two or more compounds, formed by the strong hydrogen bond network between its constituents, where the eutectic point is far below the melting point obtained assuming the ideal liquid phase behavior. [6]

These new mixtures can be formed by mixing biodegradable and inexpensive materials, using mild temperatures, without chemical reactions. A deep eutectic solvent depends on the start materials to be renewable. DES can be classified as designed solvents due to the structural ability to combine hydrogen bond donors (HBD) and hydrogen bond acceptors (HBA), designing and adjusting their physical properties and behavior phase. [6]

Its characteristics such as low toxicity, non-volatility, non-flammability, no reactivity with water, and biodegradability, are some of the properties that help them to be good solvents for different applications in catalysis, organic synthesis, dissolution processes, and electrochemical and chemical extraction of materials. [6]

Ozturk et al. studied the separation of essential oils through deep eutectic biorenewable solvents, composed of glycerol and choline chloride. The DES studied in this work seemed adequate to separate linalool from limonene through liquid-liquid extraction. For DES composed of glycerol during mass transfer, limitations may occur due to high viscosity, limiting the migration of terpenoids from the terpene phase to the solvent phase. To circumvent the viscosity problem, it was decided to add choline chloride in the proportion of 1:2, decreasing the viscosity. It was also studied the addition of water to the mixture of glycerol and choline chloride, but this new mixture decreased the solvent's capacity to extract limonene and linalool, this effect occurs because water decreased the solubility and impaired the extraction. Besides, water can also influence the hydrogen bonds between HBA (choline chloride) and HBD (Glycerol), impairing the interaction between DES and linalool.

2.4 Infinite dilution activity coefficients

2.4.1 Infinite dilution activity coefficients

The activity coefficients at infinite dilution (γ) provide strong evidence about the interactions between solutes and solvents. Knowledge of thermodynamic properties and phase equilibria is necessary to understand the affinity between ionic liquids and the solutes to be separated. [41] In

this way, the infinite dilution activity coefficients (γ), can be used to assess the potential of ionic liquids as mass separation agents, thus allowing the calculation of the selectivity, capacity, and partition coefficient, with this information being important for the design of an efficient separation process. [41,42] If used correctly it can be very useful in the design of chemical separation processes, such as fractional distillation, gas separation, and liquid-liquid extraction. [43]

The activity coefficients describe the degree of thermodynamic non-ideality between two substances due to intermolecular interactions. These intermolecular interactions are induced by van der Waals interactions and electrostatic interactions, either intermolecular or intramolecular, hydrogen bonding effects, consequently causing a positive or negative deviation from ideality. Attractive net interactions result in a coefficient of activity below the unit, and repulsive interactions result in an activity coefficient above the unit. The activity coefficients are dependent on the composition and a limit case is when a solute is infinitely diluted in a solvent. The non-ideal behavior of the solute at infinite dilution is induced exclusively by the solvent-solute interaction, that is, the effect of the molecular properties of the solvent on the solute activity coefficient. The activity coefficient in this limit case is called the activity coefficient of infinite dilution. [44]

The study of the activity coefficients at infinite dilution in systems with ionic liquids increases the understanding of the separation of mixtures with nearby boiling points. Important information about interactions between solutes and molecules of ionic liquids can be obtained for separation. [43]

Seeking to expand knowledge about the separation of compounds through the combination of mixtures of ionic liquids, and due to the difficulty of finding experimental measurements in the literature, the activity coefficients at infinite dilution were studied, as well as the selectivity and capacity values for specific separation problems can be calculated based on the activity coefficients. [43]

Martins et al. used the ionic liquids $[C_4mim]Cl$, $[C_4mim][CH_3SO_3]$, $[C_4mim][(CH_3)_2PO_4]$, and $[C_4mim][CF_3SO_3]$ for the temperature range from 398.15 to 448.15 K. In this work sought to validate the COSMO-RS computational methods in which it can be observed that the selectivities

obtained through COSMO-RS were generally lower than the experimental ones and the capacities were generally greater than the experimental ones. It was also found that the COSMO-RS method can be used to estimate the capacity and selectivity correctly for terpenes and terpenoids. The less polar ionic liquids were the ones that had better selectivities and capacities according to the experimental results. The most relevant results found by Martins et al. were presented for polar anions, bis(2,4,4-trimethylpentyl)phosphinate, or acetate reaching greater selectivities, to obtain the best separation capacities for non-polar cations such as the phosphonium base is more suitable. Thus, it can be concluded that to improve the selectivity and capacity of the separation processes of terpenes and terpenoids, cations and anions with different characteristics must be used. [4]

In previously works, ionic liquids based on imidazolium have been studied as separation agents and impurity removal from terpenes. Vilas-Boas et. al. measured the activity coefficients at infinite dilution in [C_4min][OAc], [$P_{6,6,6,14}$][(C_8H_{17})$_2PO_2$] and [$P_{6,6,6,14}$]Cl, in the temperature range from 333.15 to 453.15 K. It was found that for less polar solutes in ionic liquids [C_4min][OAc], the activity coefficient the infinite dilution increases compared to [$P_{6,6,6,14}$][(C_8H_{17})$_2PO_2$] or with [$P_{6,6,6,14}$]Cl. [14]

2.4.2 Determination of infinite dilution activity coefficients

Currently, there are different methods to determine the activity coefficient. In this work, the gas chromatography (GC) method will be applied. The GC is often used when the sample amount is very small, which is introduced in the column with a non-volatile stationary phase, the calculation of the activity coefficient in infinite dilution, γ_{13}^{∞}, can be performed between the carrier gas and the non-volatile liquid solvent, through solute retention [13], using the equation developed by Everett [45] and Cruickshank et al. [46]:

$$\ln(\gamma_{13}^{\infty}) = \ln\left(\frac{n_3 RT}{V_N P_1^*}\right) - \frac{P_1^*(B_{11} - V_1^*)}{RT} + \frac{P_o J_2^3 (2B_{12} - V_1^{\infty})}{RT} \tag{1}$$

where:

n_3 is the number of moles of solvent on the column packing;

T is the GC oven absolute temperature where the column is placed;

V_N is the net retention volume of the solute;

P_1^* is the saturated vapor pressure of the solute a T;

B_{11} is the second virial coefficient of the pure solute;

V_1^* is the molar volume of the solute;

P_o is the column outlet pressure;

J_2^3 is a pressure correction term;

B_{12} is the mixed second virial coefficient of the solute and the carrier gas;

V_1^∞ is the partial molar volume of the solute at infinite dilution in the solvent.

The pressure correction term J_2^3 and V_N, was discussed in detail by Everett [45] and Blumberg [47] are expressed by Equations 2 and 3, respectively:

$$J_2^3 = \frac{2}{3} \frac{(P_i/P_o)^3 - 1}{(P_i/P_o)^2 - 1} \tag{2}$$

where, P_i is the inlet pressure of the column. The net retention volume of the solute, V_N, is given by

$$V_N = \frac{U_0(t_s - t_g)}{J_2^3} \tag{3}$$

where, t_s and t_g are the measured retention time of the solute are obtained from a reference substance not retained by the stationary phase, usually, the air is injected at the same time as the solute. The volumetric flow, U_0, is measured after the carrier gas passing through the detector, so it is necessary to use Equation 4 to correct the flow.

$$U_0 = U \frac{P_M}{P_o} \frac{T}{T_M} \tag{4}$$

The values of volumetric flow, U, pressure, P_M and temperature, T_M, are measured by the flowmeter. To calculate the outlet pressure of the column, P_0, a linear correlation was established between the pressure drop values ΔP and the volumetric flow for different temperatures, using Equation 5 presented below.

$$\Delta P = P_o - P_M = AU + B \tag{5}$$

From the infinite dilution activity coefficients, partial properties such as excess Gibbs energy $\bar{G}_m^{E,\infty}$, enthalpy $\bar{H}_m^{E,\infty}$, and entropy $\bar{S}_m^{E,\infty}$ can be calculated using Equation 6, 7, and 8, respectively:

$$\bar{G}_m^{E,\infty} = RT ln(\gamma_{13}^\infty) \tag{6}$$

$$\bar{H}_m^{E,\infty} = R \left[\frac{\partial \, ln(\gamma_{13}^\infty)}{\partial (1/T)} \right]_{p,x} \tag{7}$$

$$\bar{S}_m^{E,\infty} = \frac{\bar{H}_m^{E,\infty} - \bar{G}_m^{E,\infty}}{T} \tag{8}$$

2.4.3 Selectivity and Capacity

The values of selectivity and capacity for any separation problem can be obtained from the activity coefficient at infinite dilution using Equations 9 and 10, respectively.

$$S_{ij}^\infty = \frac{\gamma_i^\infty}{\gamma_j^\infty} \tag{9}$$

$$k_j^\infty = \frac{1}{\gamma_j^\infty} \tag{10}$$

where the subscripts i e j represent the solutes, j being the solute with the lowest value of activity coefficient for a given separation.

2.5 Forecasting methodology

The simulation methods are interesting because they allow predicting interactions, and behaviors with greater ease. COnductor-like Screening MODEL for Real Solvents (COSMO-RS) is a well-defined method for predicting the thermophysical properties of fluids and mixtures of liquids. This method uses the quantum chemical characterization of solute and solvent molecules with thermodynamic statistical analysis, surface interactions, in this way it becomes possible to predict the thermodynamic properties of mixing liquids. [48,49] It is possible to find more information about the method as its theoretical basis in the works. [48,50–52] To use the model, it is only necessary to know the structure, electronic energy, and polarization charge density (ρ) to each component, based on this information, COSMO-RS predicts the chemical potential of the compound. [14] The activity coefficients at infinite dilution are obtained directly from the chemical potential for this method. [14,52] COSMO-RS is being widely used to predict experimental data on fluids such as water, organic solutes in liquid solvents, and also for ionic liquids.
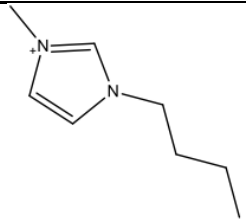
Vilas-Boas et. al, used COSMO-RS to predict thermophysical data of ionic liquids trihexyl (tetradecyl) phosphonium chloride ($[P_{6,6,6,14}]Cl$), trihexyl(tetradecyl)phosphonium bis (2,4,4-trimethylpentyl) phosphinate ($[P_{6,6,6,14}][(C_8H_{17})_2PO_2]$) and 1-butyl-3-methylimidazolium ($[C_4mim][OAc]$) including selectivity and capacity for terpene fractionation problems, which obtained values in agreement with the experimental data for most terpene/terpene separation studied. Is experimentally proven that the model also shows for some mixtures between terpenes and terpenoids in ionic liquids, a greater fractionation potential is obtained to separate several essential oils impurities from fossil fuels. [14]

Chapter 3. Experimental work

3.1 Chemicals

The complete list with the 40 solutes used in this work is described in Appendix B (Table B.1). The ionic liquids used were, 1-dodecyl-3-methylimidazolium, ([C_{12}mim]Cl) (CAS Number: 171058-18-7) and an equimolar mixture of 1-butyl-3-methylimidazolium ([C_4mim]Cl) (CAS Number: 79917-90-1), and 1-dodecyl-3-methylimidazolium ([C_{12}mim]Cl), respectively. The structure, supplier, molar mass, and purity are described in Table 1, below:

Table 1 – Ionic liquid, chemical name, structure, source, molar mass (M), and purity.

Chemical Formula		Chemical name	Supplier	M (gmol^{-1})	Purity (mass %)
Cation	Anion				
	Cl-	1-butyl-3-methylimidazolium chloride - [C_4mim]Cl	IoLitec	174.67	99

The solutes used during this work were separated into groups belonging to diverse functional groups, alkanes, cycloalkanes, ketones, ethers, cycloethers, aromatic hydrocarbons, esters, acetonitrile, pyridine, thiophene, water, alcohols, terpenes, terpenoids, and considering their volatility. As shown in Table 2, below:

Table 2 – Groups of solutes.

Group 1	Group 2
heptane	methanol
octane	ethanol
nonane	1-propanol
decane	2-propanol
cyclohexane	1-butanol
methyl cyclohexane	2-butanol
benzene	iso-butanol
toluene	tert-butanol
ethylbenzene	water
p-xylene	α-pinene
thiophene	β-pinene
THF	A-pinene oxide
1,4-dioxane	eucalyptol
diethyl ether	(-)-menthone
acetone	p-cymene
butanone	R(+)-limonene
methyl acetate	(R)-(-)-fenchone
ethyl acetate	γ-terpinene
vinyl acetate	myrcene
pyridine	
acetonitrile	

3.2 Experimental method

In this work, a Varian CP-3380 gas chromatograph (GC), equipped with a 1041 column heated injector and a thermal conductivity detector (TCD), was used to measure the retention times of the solute t_s and the non-retained gas t_g, respectively. The chromatographic columns were prepared in collaboration with the CICECO laboratory at the University of Aveiro. The column preparation and packaging procedure is described in the works [4,53] The stationary phase was prepared by mixing 45 to 55% by mass of Chromosorb W/AW-DMSC (100-120 mesh) with the ionic liquid. The chromosorb was mixed with the ionic liquid, then dissolved the mixture in methanol under constant stirring, evaporated the solvent until the original mass of the mixture was obtained (uncertainty within ± 1 x 10^{-4} g). After this process, a glass column (4 mm internal

diameter and 1 meter long) was filled with the stationary phase and placed in the GC oven. Before starting the experiments, the column was preconditioned, passing helium gas through the column, at 333.15 K for four hours, to remove any contaminants. The inlet pressure (Pi) at the column inlet was measured by a Swagelok S Model Transducer with 0.5% accuracy of the calibration of the amplitude limit point. The carrier gas used was helium with an Agilent Technologies precision gas flow meter (Part number 5973-1712) was placed after the TCD to measure volumetric flow (U), Temperature (T_M), and pressure (P_M) of that outflow. The accuracy of the equipment is $\pm$ 1.0 cm³.min^{-1} for volumetric flow, $\pm$ 0.01 K for temperature, and $\pm$ 0.01 psia for pressure. The injector and TCD temperatures were adjusted according to the boiling point temperature of the solutes, as shown in Table 3 below.

Table 3 – Injector temperature for each group of solutes.

	Temperature (K)	
	Injector	TCD
Group 1	$333.15 - 383.15$	523.15
Group 2	$373.15 - 423.15$	523.15

Setpoint temperatures are maintained for at least 30 minutes before the start of measurements. The volumetric flow was adjusted according to the retention times between the solute and the non-retained gas $t_s - t_g$ for both group the flow of approximately 60 cm³.min^{-1}. To reach the state of infinite dilution, the volume of injected solute was approximately 0.2 µL for the solutes and the remaining volume was made up of air until it reached approximately 1.0 µL.

Two chromatographic columns were prepared for each ionic liquid, the first column being used for testing, to find out how some solutes from each group interact with ionic liquids, where 12 of the 40 solutes were tested, to obtain γ_{13}^{∞} data at three different temperatures as shown in Table 4, below:

Table 4 – Temperature for the testing column.

Group	Temperature (K)
Group 1	343.15; 363.15; 383.15
Group 2	383.15; 393.15; 403.15

The second column was fully tested, with all 40 solutes being injected, obtaining γ_{13}^{∞} for at least five oven temperatures, increasing by 10 K at a time. The temperatures for performing the tests by functional groups for the main column are shown in Table 5, below:

Table 5 – Temperature for the main column.	
Group	Temperature (K)
Group 1	333.15 – 383.15
Group 2	373.15 – 423.15

3.3 Experimental results

3.3.1 Activity coefficient at infinite dilution

Due to the high boiling temperatures for some terpenes and terpenoids, degradation of the ionic liquid at high temperatures limited the measurement of the activity coefficients at infinite dilution for all solutes, however, it was tried to measure the γ_{13}^{∞} for six different temperatures for the most compounds. The values of γ_{13}^{∞} are shown in Appendix A (Tables A.1 and A.2).

Seeking to exploit the values obtained experimentally for the activity coefficient at infinite dilution, the temperature of 383.15 K, and compared the values γ_{13}^{∞}, for the pure liquid and the mixture and also considering the carbon number for each solute, as shown in Figure 1.
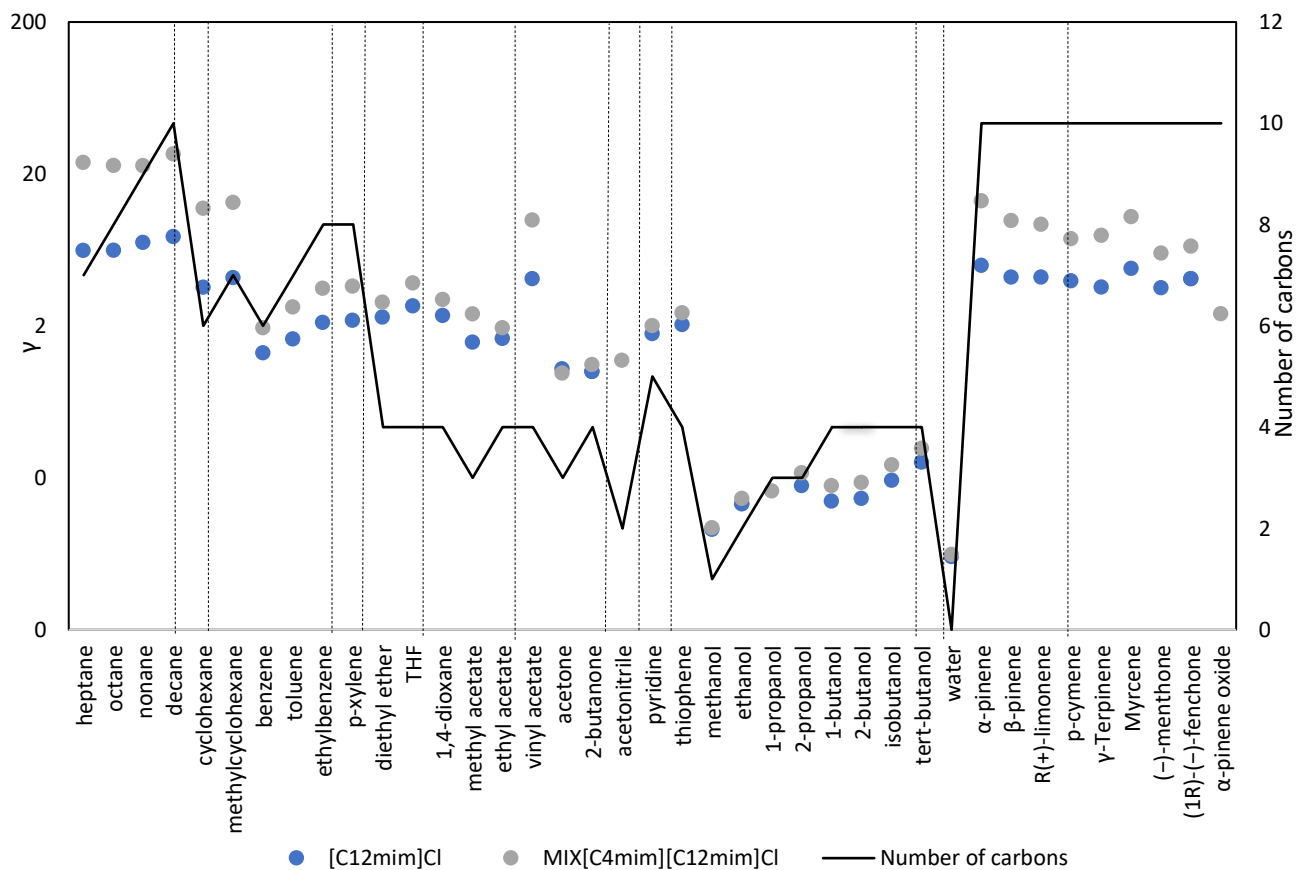
Figure 2 – Activity coefficient at infinite dilution for all solutes for both ionic liquids. The solid line represents the number of carbons in the solute structure and the dot lines represent different families.

For most solutes the γ_{13}^{∞} increased when the number of carbons in the solute structure was higher, it is also possible to verify that for some families there was greater interaction with ionic liquids.

The linear relationship between the $\ln(\gamma_{13}^{\infty})$ and $1/T$ showed good fits for most solutes, but for a few, there were some experimental inaccuracies. It is possible to observe a different behavior for the different categories of solutes: nonpolar (NP), polar and non-associative (NA), and polar and self-associative (AS). A molecule is classified as self-associative, when it must have both acceptors and donors of hydrogen bonds, on the other hand, the non-associative polar molecule has only acceptors or donors of hydrogen bonds.

The relations are shown in the Figures 3 to 34, below for the relation of $\ln(\gamma_{13}^\infty)$ to $1/T$ can be interpreted as follows, for $\ln(\gamma_{13}^\infty)$ less than zero, the deviation from ideality is negative when the value of $\ln(\gamma_{13}^\infty)$ is close to zero, it means that the solute does not have a deviation from ideality, and finally, when the value of $\ln(\gamma_{13}^\infty)$ is greater than zero implies a deviation from positive ideality. According to this interpretation, the activity coefficients at infinite dilution, the lower the value of $\ln(\gamma_{13}^\infty)$, suggests that the greater interaction between the molecules of the ionic liquid with the solute than between the molecules of the solute with itself.

The solutes that belong to the non-polar group (NP) such as the alkanes and aromatic hydrocarbons have been observed very subtle or even null slopes in some cases. For the group belonging to non-associative polar solutes (NA) such as acetonitrile, ketones, and esters, zero or positive slope was observed. Finally, for self-associating polar solutes such as alcohols and water, there was a smaller slope for alcohols and a sharp slope for water. Figures 3 and 4 show the representation of $\ln(\gamma_{13}^\infty)$ versus $1/T$ for six solutes Nonane (n-alkanes), Toluene (aromatic hydrocarbons), diethyl ether (ether), acetone (ketone), ethyl acetate (ester), and α-pinene (terpene) representing their respective families in the ionic liquid [C$_{12}$mim]Cl and in the equimolar mixture between [C$_4$mim]Cl and [C$_{12}$mim]Cl. It is worth noting that the slopes of the straight line remain similar for both cases, but the values of $\ln(\gamma_{13}^\infty)$ can vary significantly.
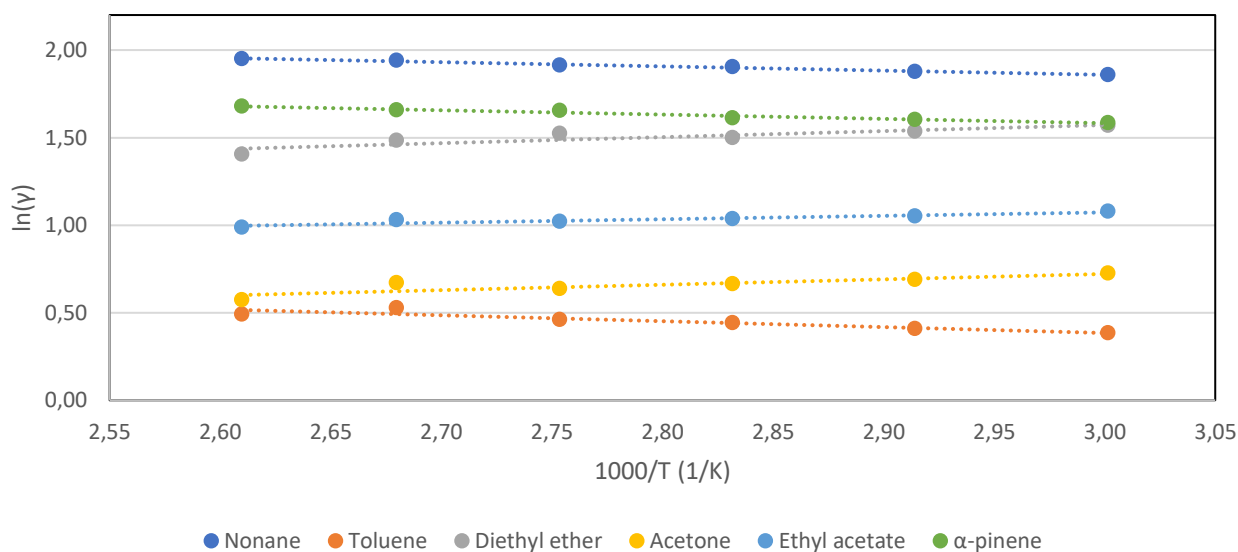
Figure 3 - $\ln(\gamma_{13}^{\infty})$ versus $1/T$ for several solutes in [C$_{12}$mim]Cl. For nonane, toluene, diethyl ether, acetone, ethyl acetate, and α-pinene.
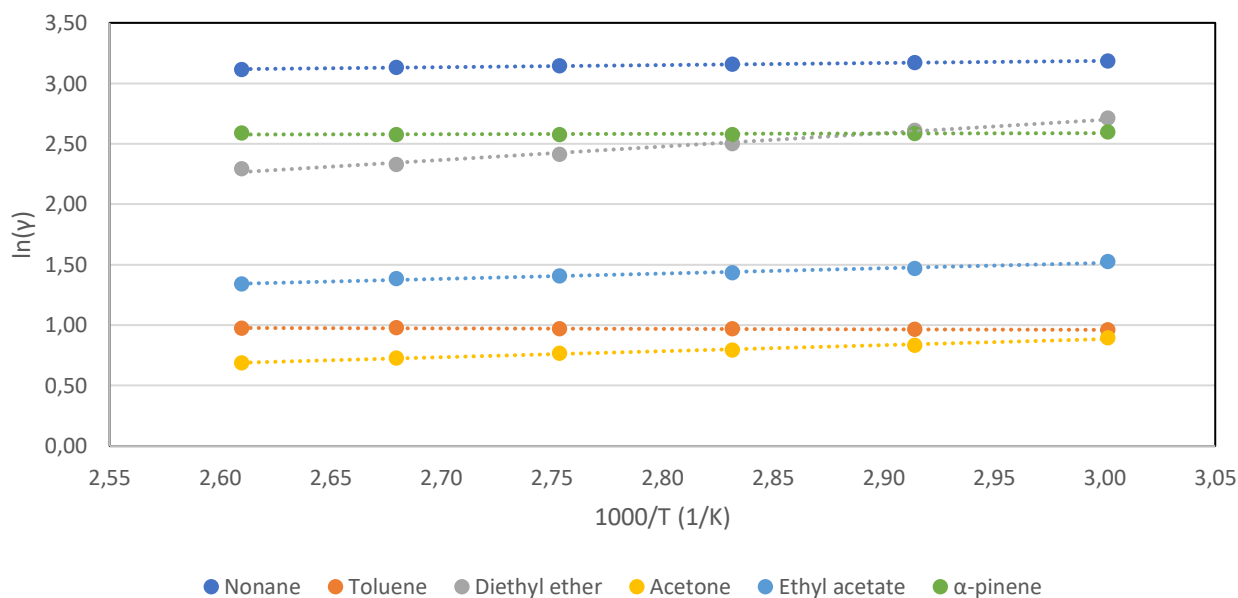
Figure 4 - $\ln(\gamma_{13}^{\infty})$ versus $1/T$ for several solutes in MIX[C$_4$mim][C$_{12}$mim]Cl. For nonane, toluene, diethyl ether, acetone, ethyl acetate, and α-pinene.

Evaluating Figures 3 and 4, we can say that the interactions between the solutes and the pure ionic liquid and the mixture of ionic liquids are different, in general for the mixture for ionic liquids the $\ln(\gamma_{13}^{\infty})$ are higher than pure ionic liquid, this could mean that the solute interacts more with the mixture than pure ionic liquid. The solutes with a higher increase of interactions for the mixture

of ionic liquids are nonane following by α-pinene, and the less increase is showed for acetone, it is could be explained for column polarity, which the mixture of ionic liquids is less polar than pure ionic liquid, and for the higher interactions for compounds less polar.

Very defined patterns were observed among the solutes of the same family, as shown in Figures 5 and 6 for alkanes and aromatic hydrocarbons.

Figure 5 - ln (γ_{13}^{∞}) versus $1/T$ for several solutes in [C$_{12}$mim]Cl. For heptane, octane, nonane, decane, benzene, ethylbenzene and toluene.

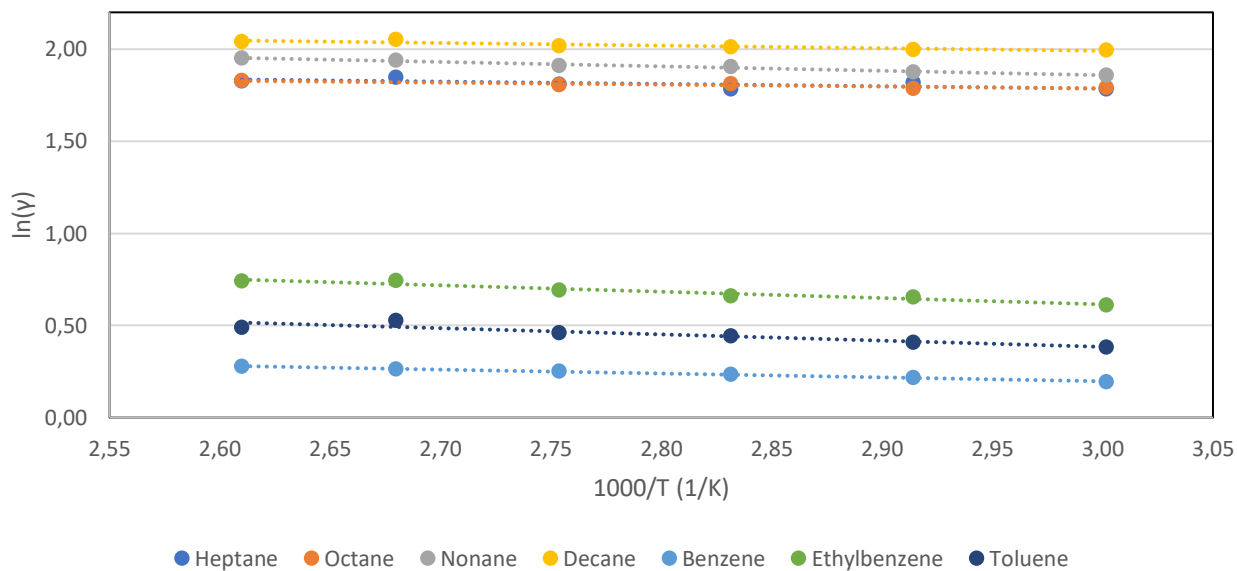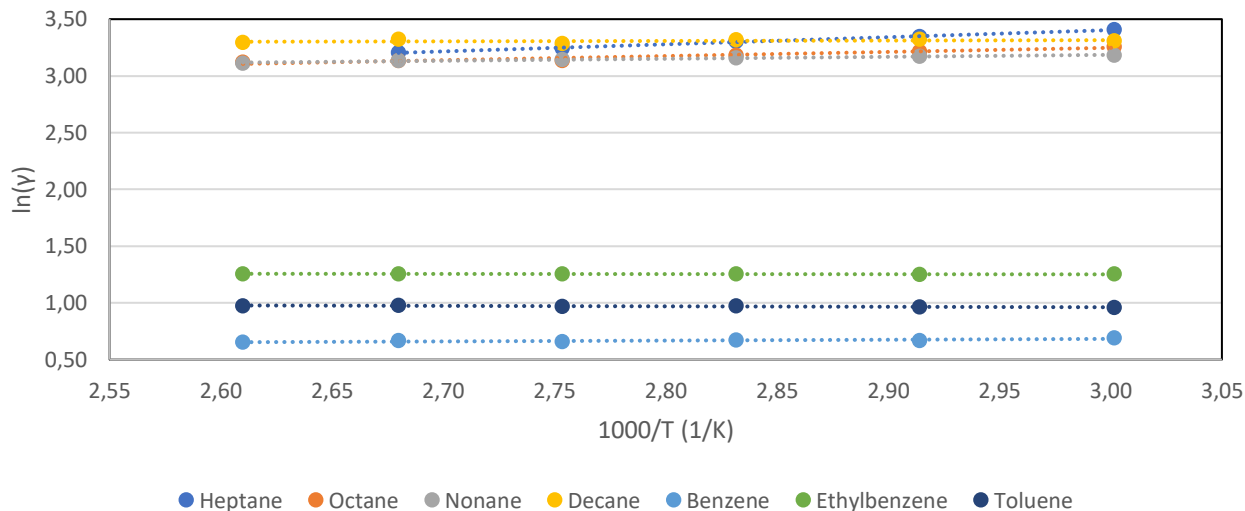**Figure 6** - ln (γ_{13}^{∞}) versus $1/T$ for several solutes in MIX[C$_4$mim][C$_{12}$mim]Cl. For heptane, octane, nonane, decane, benzene, ethylbenzene and toluene.

N-alkanes and aromatic hydrocarbons are classified as non-polar, but aromatic hydrocarbons are more polarizable than n-alkanes, due to the interactions of π electrons. It is possible to observe this difference experimentally in the lower values of ln (γ_{13}^{∞}), indicating a higher interaction with ionic liquids. It is possible to better observe this difference in Figures 7 and 8 were the ln (γ_{13}^{∞}) of cycloalkanes and aromatic hydrocarbons are presented.
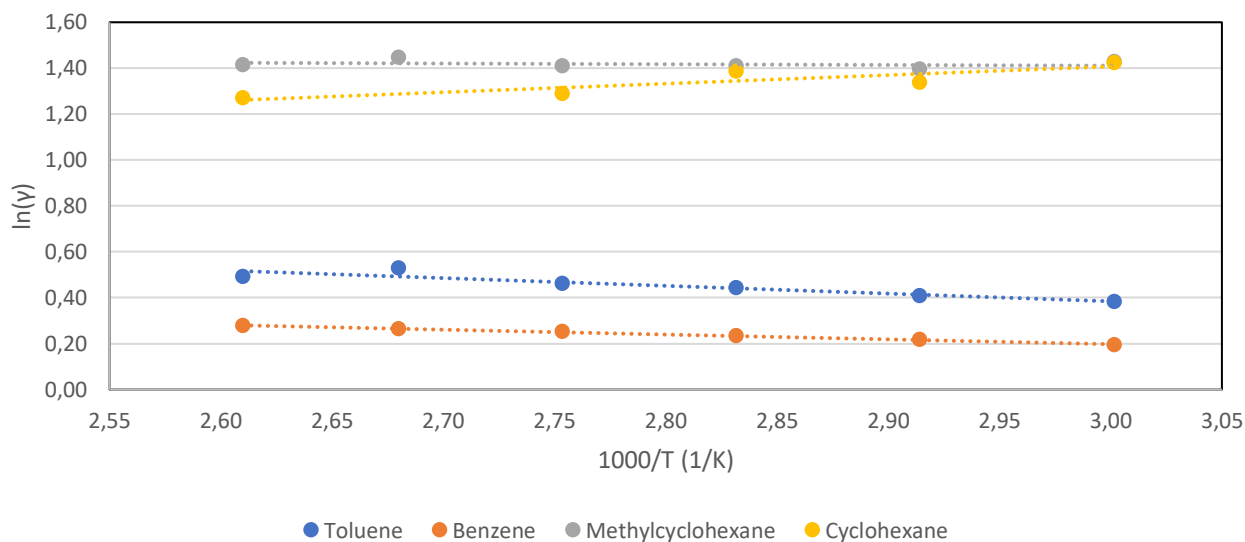

Figure 7 - ln (γ_{13}^{∞}) versus $1/T$ for several solutes in [C$_{12}$mim]Cl. For toluene, benzene, methylcyclohexane, and cyclohexane
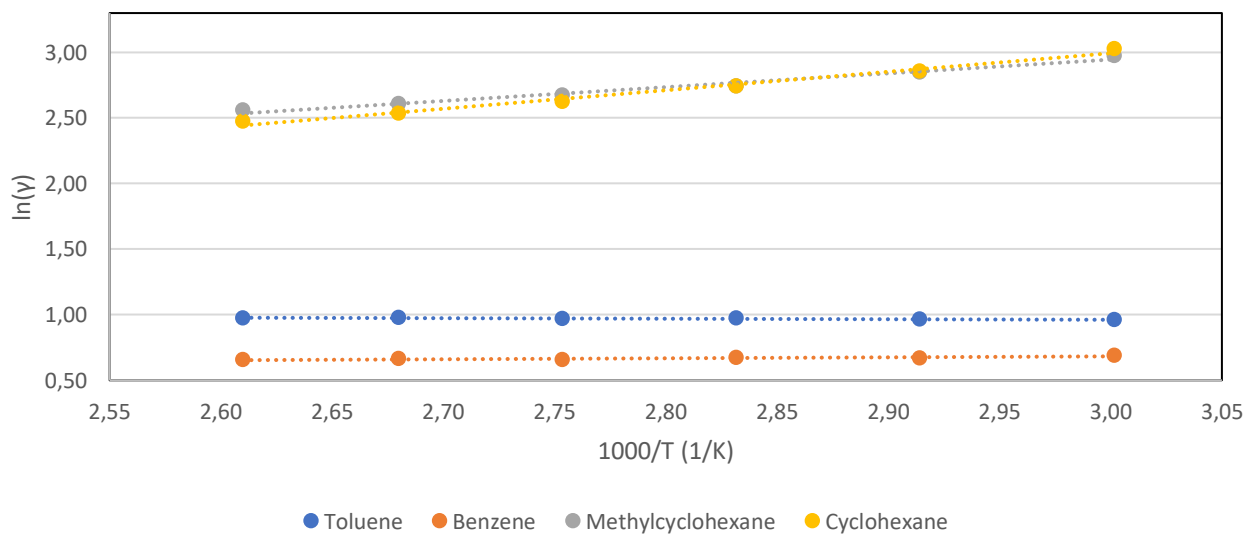
Figure 8 - ln(γ_{13}^{∞}) versus $1/T$ for several solutes in MIX[C$_4$mim][C$_{12}$mim]Cl. For toluene, benzene, methylcyclohexane, and cyclohexane

Observing Figures 7 and 8 the activity coefficients of infinite dilution of toluene and benzene are lower than those of methylcyclohexane and cyclohexane for both ionic liquids. For the methylcyclohexane and cyclohexane solutes, greater interaction with the mixture of ionic liquids [C$_4$mim][C$_{12}$mim]Cl has been observed than with pure ionic liquid [C$_{12}$mim]Cl, the same was observed for n-alkanes compared to aromatics. Illustrating the same behavior described above, Figures 9 and 10 show the ln(γ_{13}^∞) for toluene, benzene, ethylbenzene, and p-xylene (aromatic hydrocarbons) with different numbers of carbon atoms.
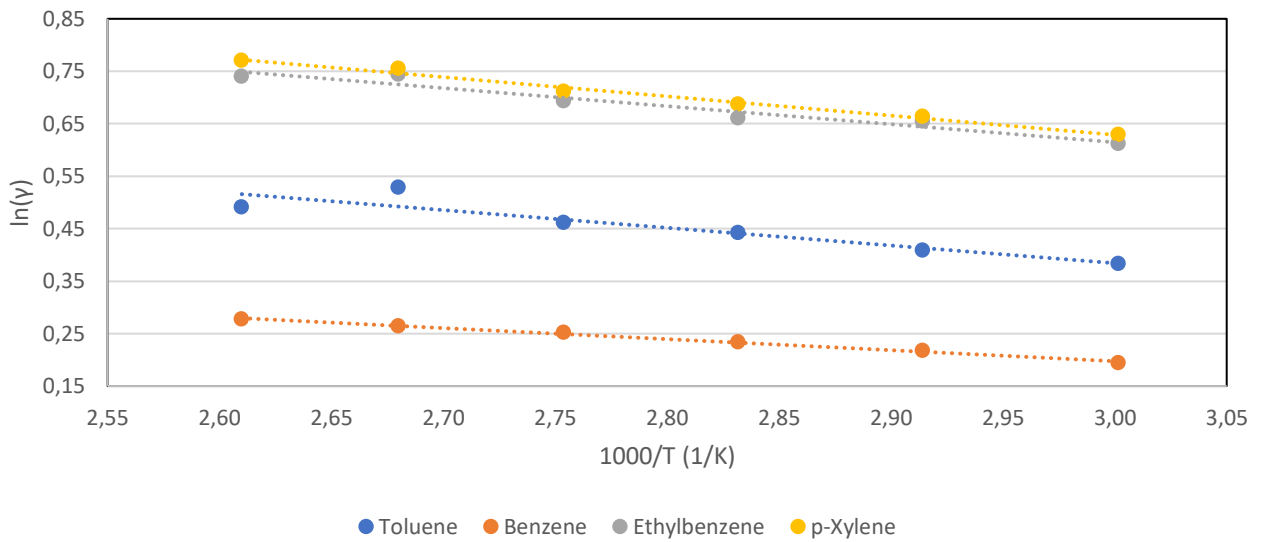
Figure 9 - ln(γ_{13}^∞) versus $1/T$ for several solutes in [C$_{12}$mim]Cl. For toluene, benzene, ethylbenzene and p-xylene.
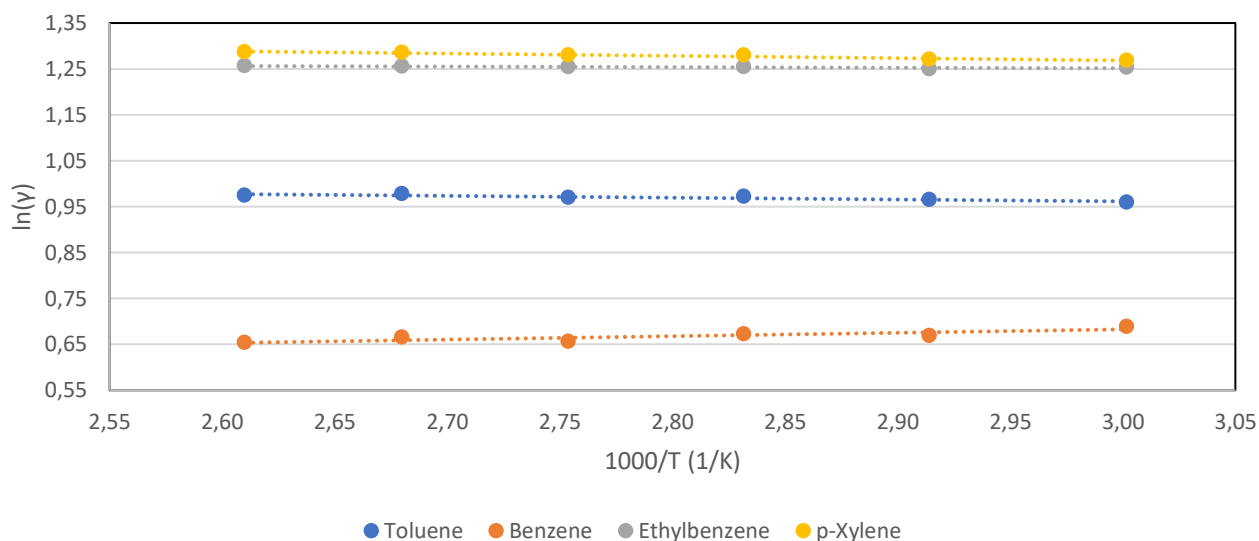
Figure 10 - $\ln(\gamma_{13}^{\infty})$ versus $1/T$ for several solutes in MIX[C$_4$mim][C$_{12}$mim]Cl. For toluene, benzene, ethylbenzene and p-xylene.

In the figures above, it is possible to observe that the carbon atoms outside the aromatic ring contribute to the increase in the value of $\ln(\gamma_{13}^{\infty})$. For both ionic liquid values of $\ln(\gamma_{13}^{\infty})$ for p-xylene were slightly higher than for ethylbenzene. Figures 11 and 12 show the values obtained for the ether group in the two ionic liquids.
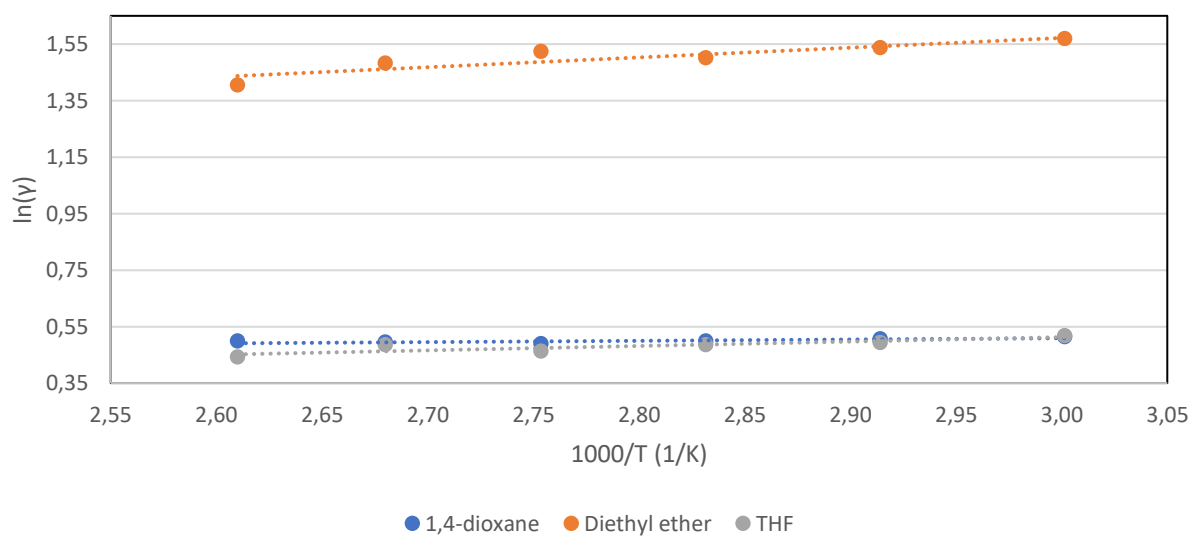
Figure 11 - $\ln(\gamma_{13}^{\infty})$ versus $1/T$ for several solutes in [C$_{12}$mim]Cl. For 1,4-dioxane, diethyl ether, and THF.
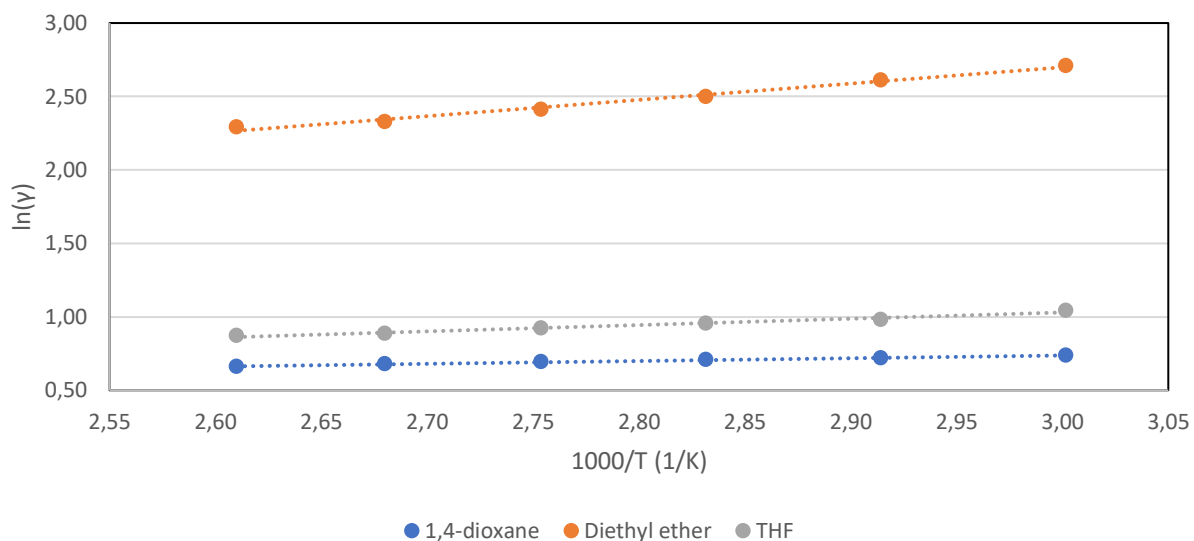
Figure 12 - $\ln(\gamma_{13}^{\infty})$ versus $1/T$ for several solutes in MIX[C_4mim][C_{12}mim]Cl. For 1,4-dioxane, diethyl ether, and THF.

For the ethers presented above diethyl ether and the THF presented $\ln(\gamma_{13}^{\infty})$ smaller in the ionic liquid [C_{12}mim]Cl than in the mixture of ionic liquids [C_4mim][C_{12}mim]Cl, while for 1,4-dioxane the values of $\ln(\gamma_{13}^{\infty})$ in the two ionic liquids were similar. Even belonging to the same class of chemical compounds, this difference in behavior can occur due to the difference of oxygen atoms in the solutes where the first two mentioned have only one oxygen atom, while the last has two. It was also possible to observe a change in the positive slope for diethyl ether if compared to the mixture of ionic liquids. For the other two solutes, the slope differences were not significant. This change in the slope may have occurred because diethyl ether is not cyclic, while the other two solutes are cyclic. Figures 13 and 14 present other oxygenated compounds for both situations.
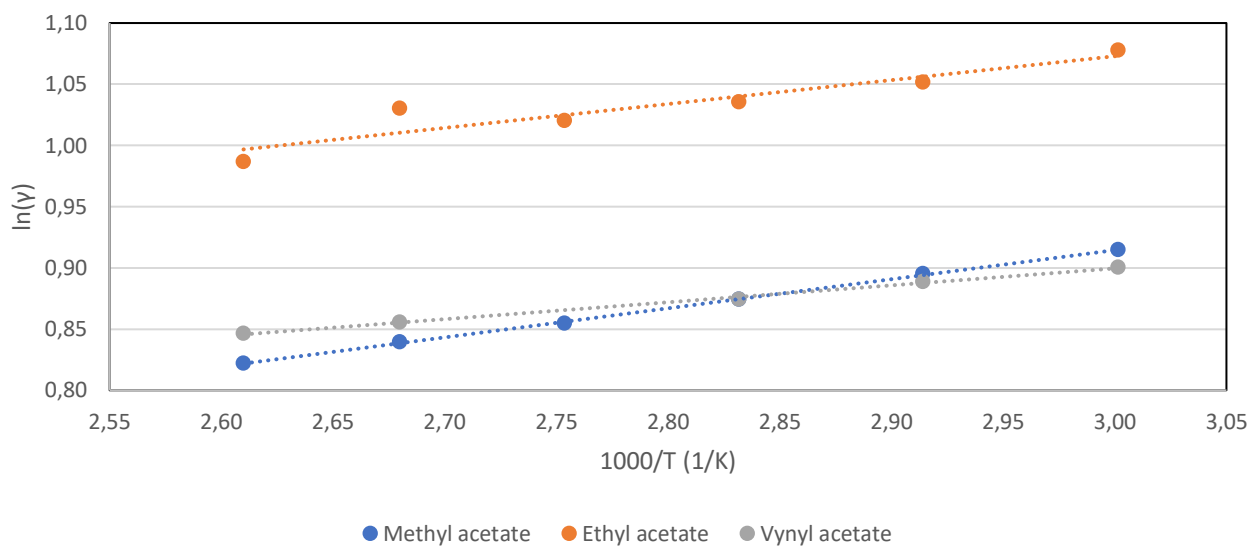
Figure 13 - ln (γ_{13}^∞) versus $1/T$ for several solutes in [C$_{12}$mim]Cl. For methyl acetate, ethyl acetate, and vinyl acetate.
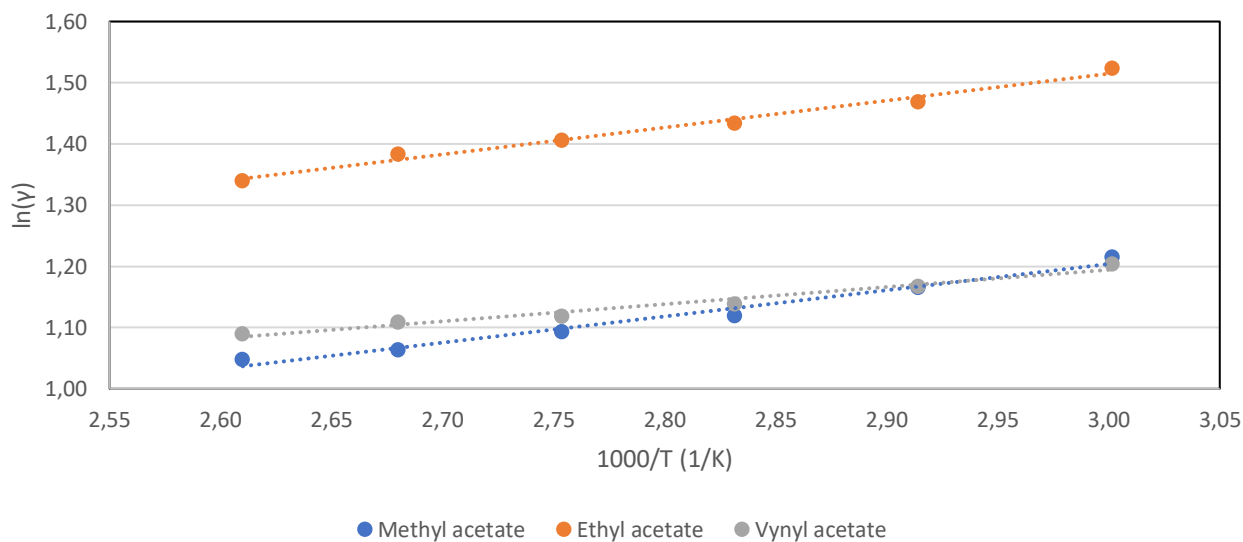
Figure 14 - ln (γ_{13}^∞) versus $1/T$ for several solutes in MIX[C$_4$mim][C$_{12}$mim]Cl. For methyl acetate, ethyl acetate, and vinyl acetate.

The esters showed, in general, greater interaction with the mixture of ionic liquids [C$_4$mim][C$_{12}$mim]Cl than with in the pure ionic liquid [C$_{12}$mim]Cl. The values of ln(γ_{13}^∞) versus $1/T$ of acetonitrile, pyridine, and thiophene are shown below in Figures 15 and 16 in which the interference of the nitrogen and sulfur atoms are observed.

Figure 15 - $\ln(\gamma_{13}^{\infty})$ versus $1/T$ for several solutes in [C$_{12}$mim]Cl. For acetonitrile and pyridine.

Figure 16 - $\ln(\gamma_{13}^{\infty})$ versus $1/T$ for several solutes in MIX[C$_4$mim][C$_{12}$mim]Cl. For acetonitrile and pyridine.

For the solutes shown in Figures 15 and 16 above, it can be seen that there was a great interaction with the ionic liquids, due to the low values of $\ln(\gamma_{13}^{\infty})$ obtained experimentally that suggest a good interaction between the solute and column of ionic liquids. However, it is interesting to note that for pyridine there was a greater interaction with pure ionic liquid and for acetonitrile, it interacted better for the mixture of ionic liquids. For both solutes, the values of $\ln(\gamma_{13}^{\infty})$ varied from positive to negative, but close to zero, which indicates a deviation from ideality are neutral. Figures 17 and 18 show the values obtained experimentally for thiophene.
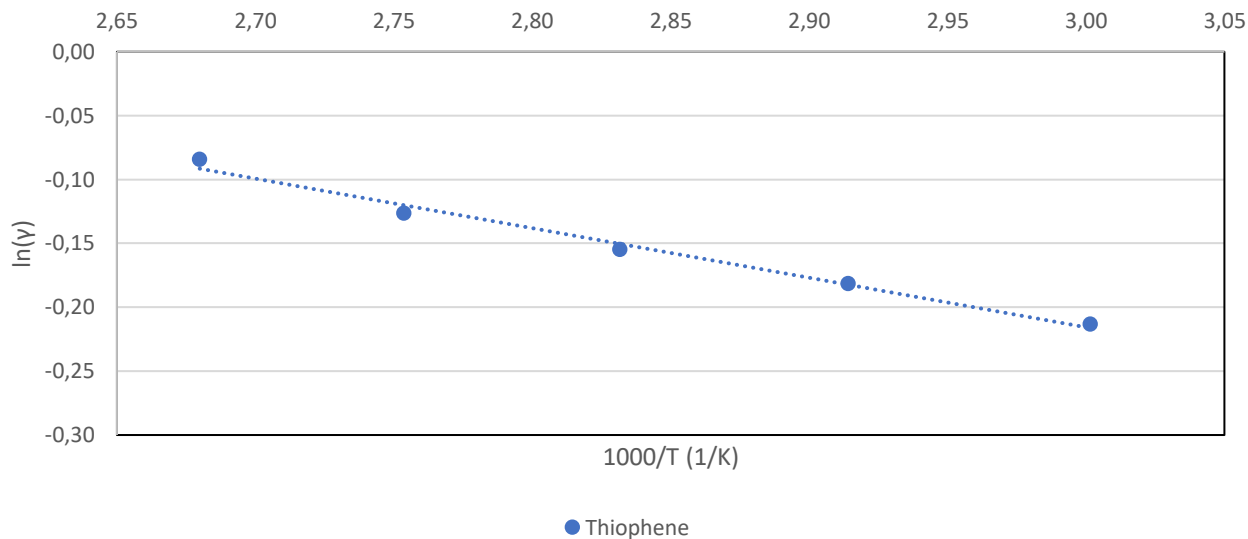
Figure 17 - ln (γ_{13}^{∞}) versus $1/T$ for the solute in [C$_{12}$mim]Cl. For thiophene.
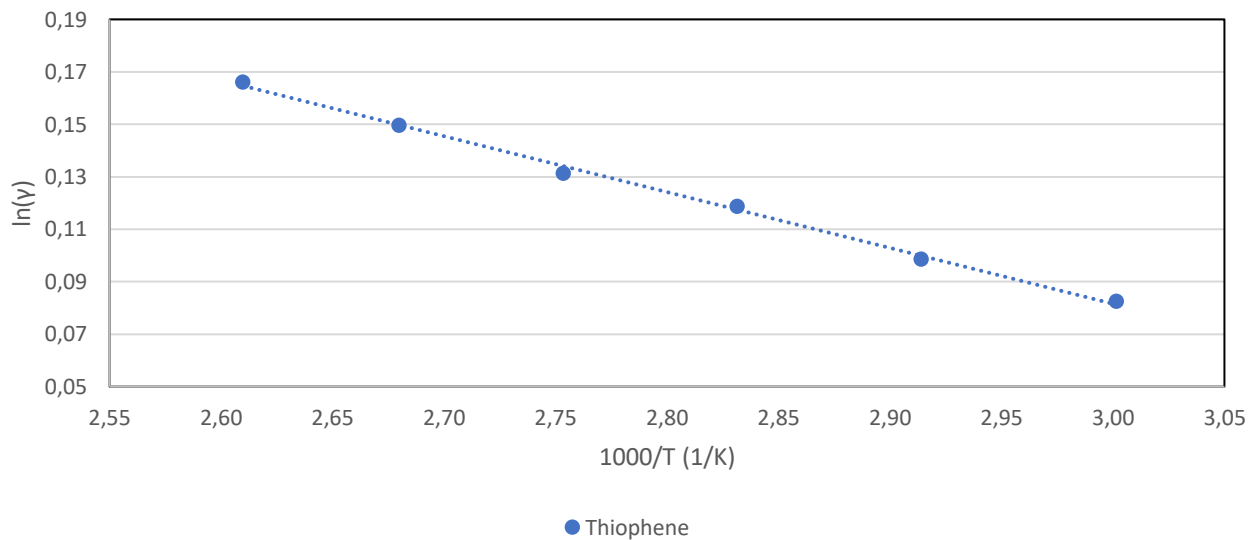
Figure 18 - ln (γ_{13}^{∞}) versus $1/T$ for the solutes in MIX[C$_4$mim][C$_{12}$mim]Cl. For thiophene.

Thiophene showed a greater interaction for [C$_{12}$mim]Cl, which can be observed by the low value of ln(γ_{13}^{∞}), which indicates that the molecules of the solute interacted better with the pure ionic liquid than with the thiophene itself. The same effect seen in Figures 15 and 16 could be observed in figure Figures 19 and 20 for butanone and acetone.
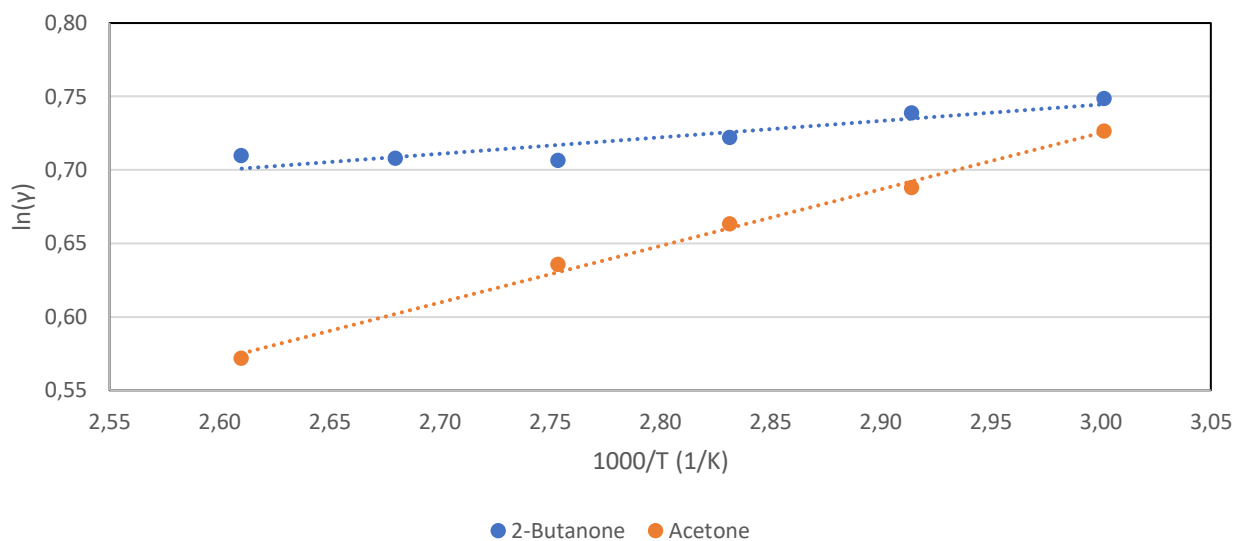
Figure 19 - $\ln(\gamma_{13}^{\infty})$ versus $1/T$ for several solutes in [C$_{12}$mim]Cl. For 2-butanone and acetone.

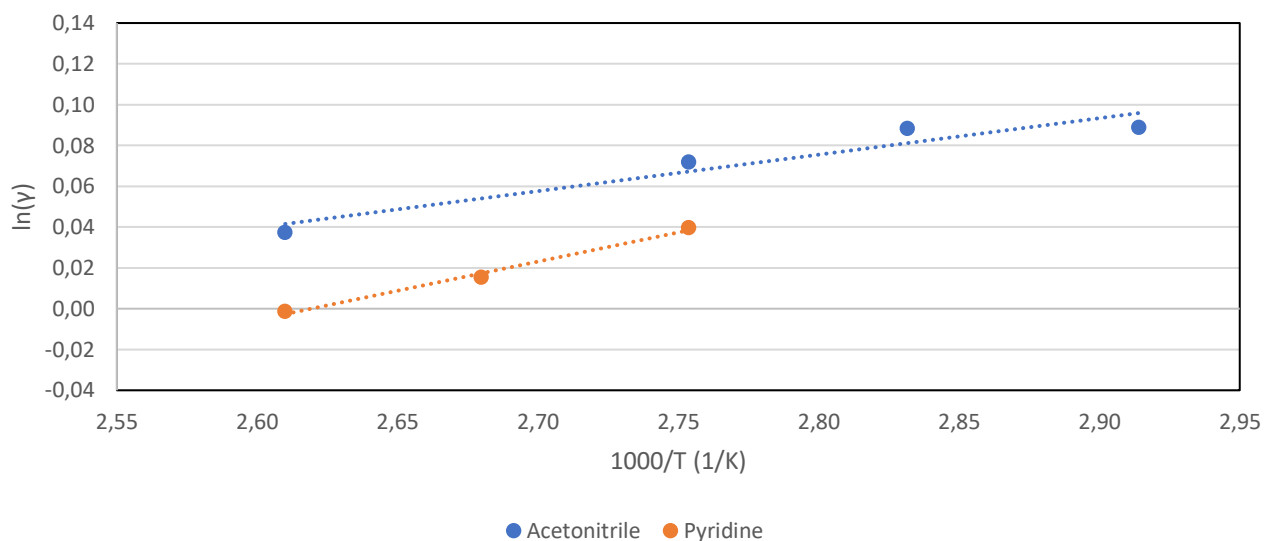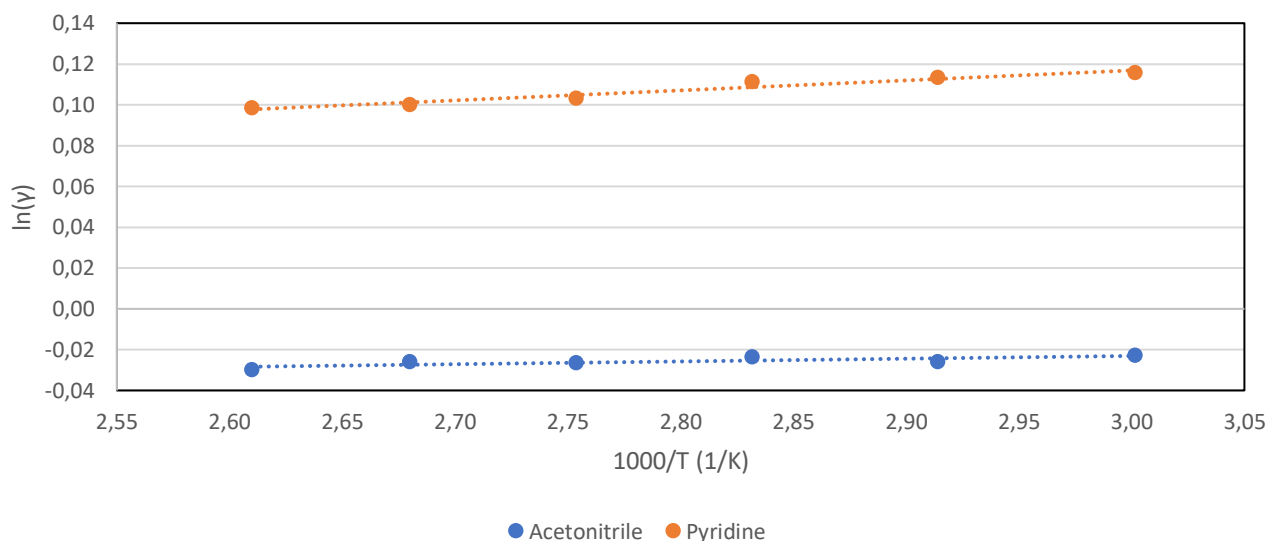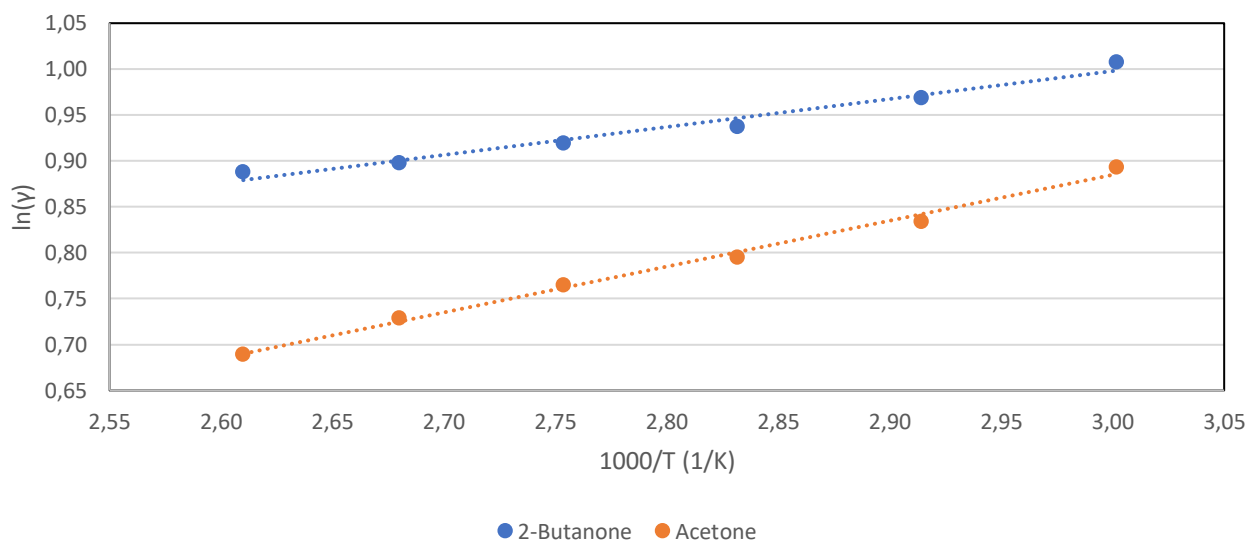**Figure 20** - $\ln(\gamma_{13}^{\infty})$ versus $1/T$ for several solutes in MIX[C$_4$mim][C$_{12}$mim]Cl. For 2-butanone and acetone.

For the two solutes butanone and acetone, they showed greater interaction with the pure ionic liquids, and how the value of $\ln(\gamma_{13}^{\infty})$ grater than zero, this indicates a positive deviation from ideality for the solutes showed above. Figures 21 and 22 show the same information in the group of alcohols for the two ionic liquids, respectively.

Figure 21 - $\ln(\gamma_{13}^\infty)$ versus $1/T$ for several solutes in [C$_{12}$mim]Cl. For methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol.

Figure 22 - $\ln(\gamma_{13}^\infty)$ versus $1/T$ for several solutes in MIX[C$_4$mim][C$_{12}$mim]Cl. For methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol.

The figures above show the $\ln(\gamma_{13}^\infty)$ for six alcohols, which can be separated into different subgroups. The formed subgroups were separated in methanol, the other primary alcohols in a second group, and finally, in the third group, the secondary alcohols. The subgroups can be better understood in Figure 21 for the pure ionic liquid, but in the mixture of ionic liquids (Figure 22), it is also possible to distinguish the separation between the subgroups, however, the difference is subtler. It is was possible to observe the alcohols present the lowest value for $\ln(\gamma_{13}^\infty)$ among all

the solutes studied in this work. The difference observed between the subgroups may occur due to the steric impediment of the hydroxyl group, mainly for the primary and secondary subgroups, and the figures showed a stronger interaction for the mixture of [C$_4$mim][C$_{12}$mim]Cl. Figures 23 and 24, present $\ln(\gamma_{13}^{\infty})$ versus $1/T$ for alcohol compounds.
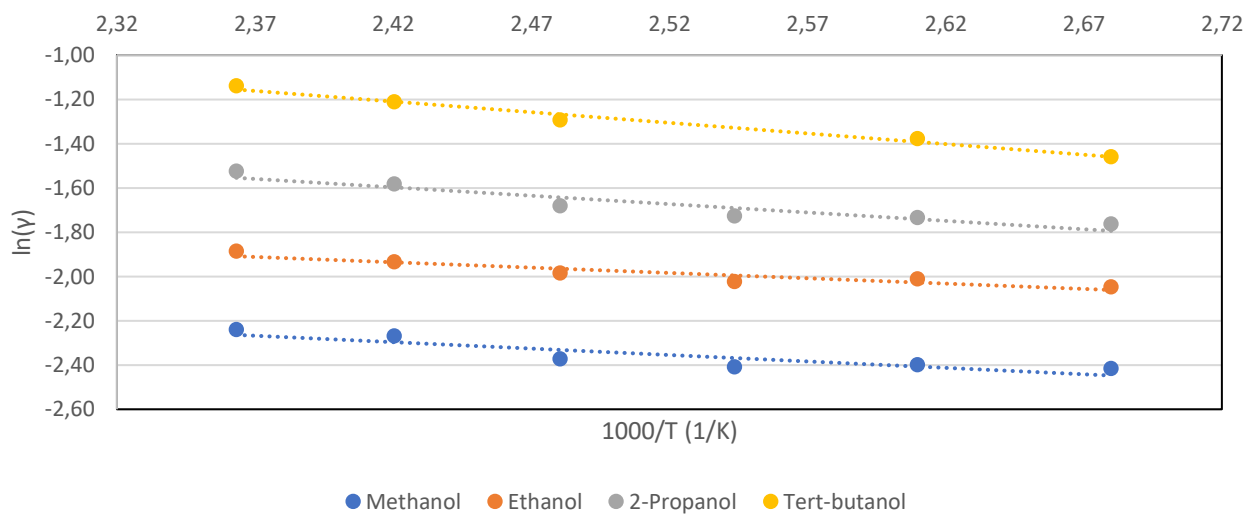
Figure 23 - $\ln(\gamma_{13}^{\infty})$ versus $1/T$ for several solutes in [C$_{12}$mim]Cl. For methanol, ethanol, 2-propanol, and tert-butanol.
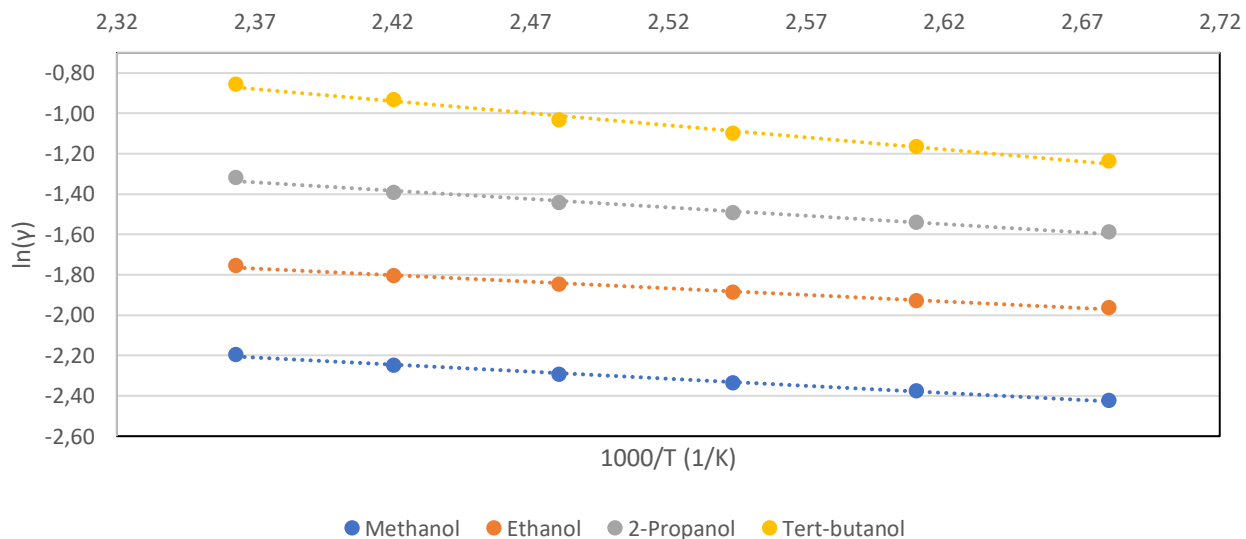
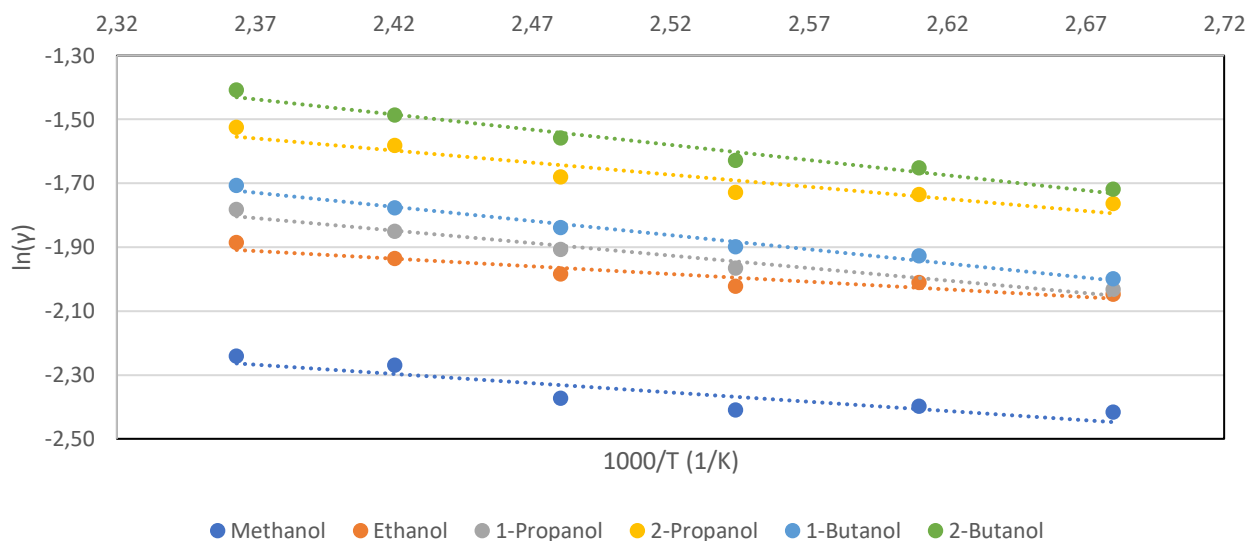**Figure 24** - $\ln(\gamma_{13}^{\infty})$ versus $1/T$ for several solutes in MIX[C$_4$mim][C$_{12}$mim]Cl. For methanol, ethanol, 2-propanol, and tert-butanol.

Observing the values of $\ln(\gamma_{13}^{\infty})$ for this group of alcohols, they are lower than all the other solutes. Only water presents even a more negative value of $\ln(\gamma_{13}^{\infty})$. However, we cannot predict what interferes most, the size of the carbon chain linked to the functional carbon, or the alcohol group (primary, secondary, and others). For both ionic liquids, the sequence was kept the same, starting with methanol, with the greatest interaction, and followed by ethanol, 2-propanol, and ending with tert-butanol (tertiary alcohol with the smaller interaction). If we compare the spacing between the primary alcohols, we can see that in Figures 21 and 22 it is smaller than those presented in Figures 23 and 24. Figures 25 and 26 show the data for butanol with different structures.
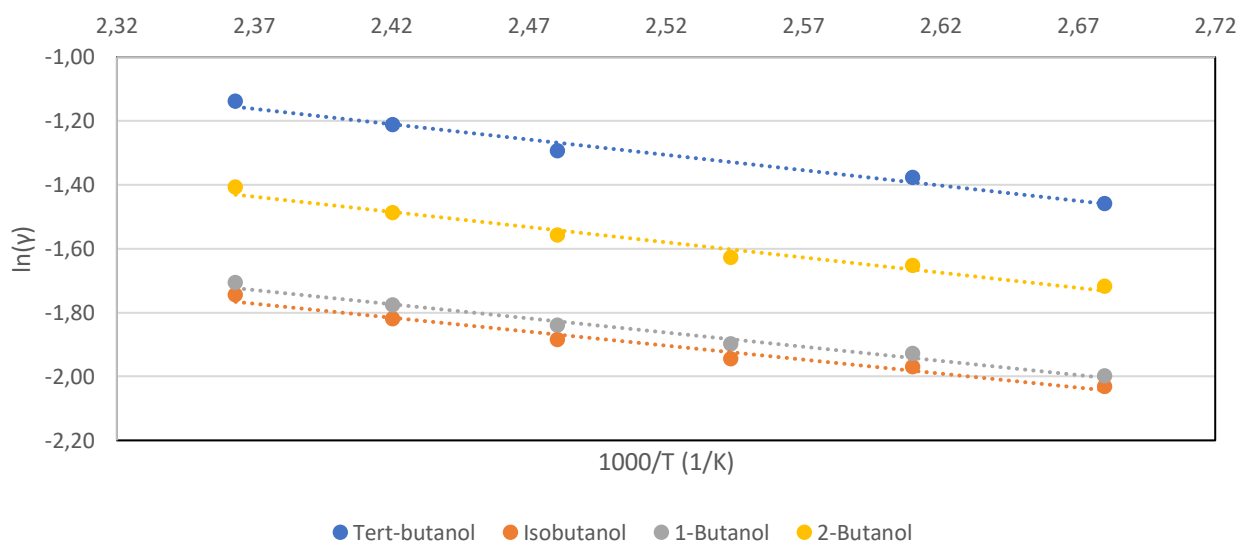
Figure 25 - $\ln(\gamma_{13}^{\infty})$ versus $1/T$ for several solutes in [C$_{12}$mim]Cl. For tert-butanol, isobitanol, 1-butanol and 2-butanol.
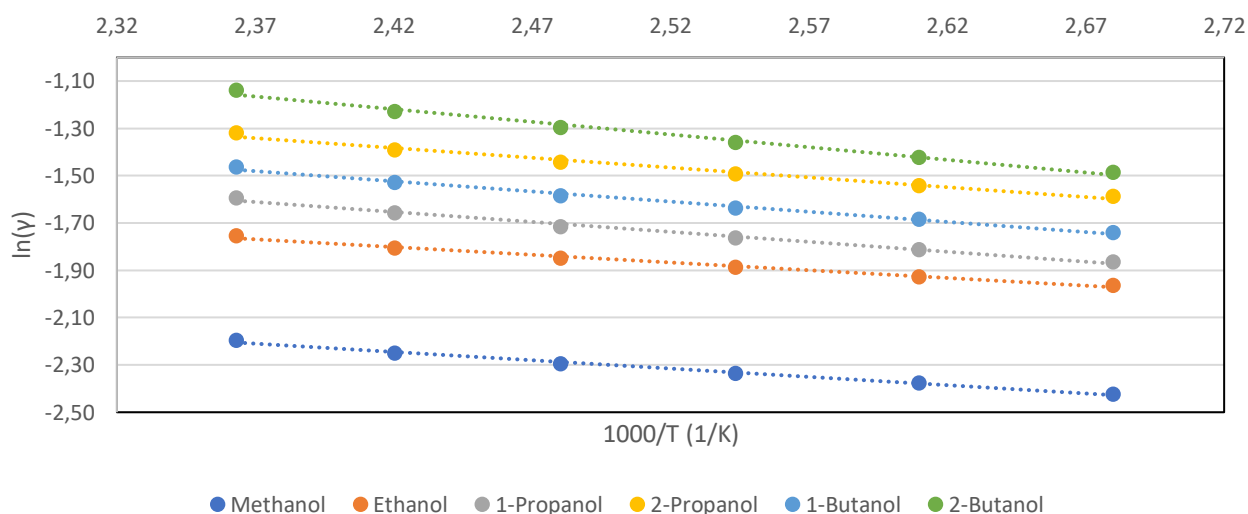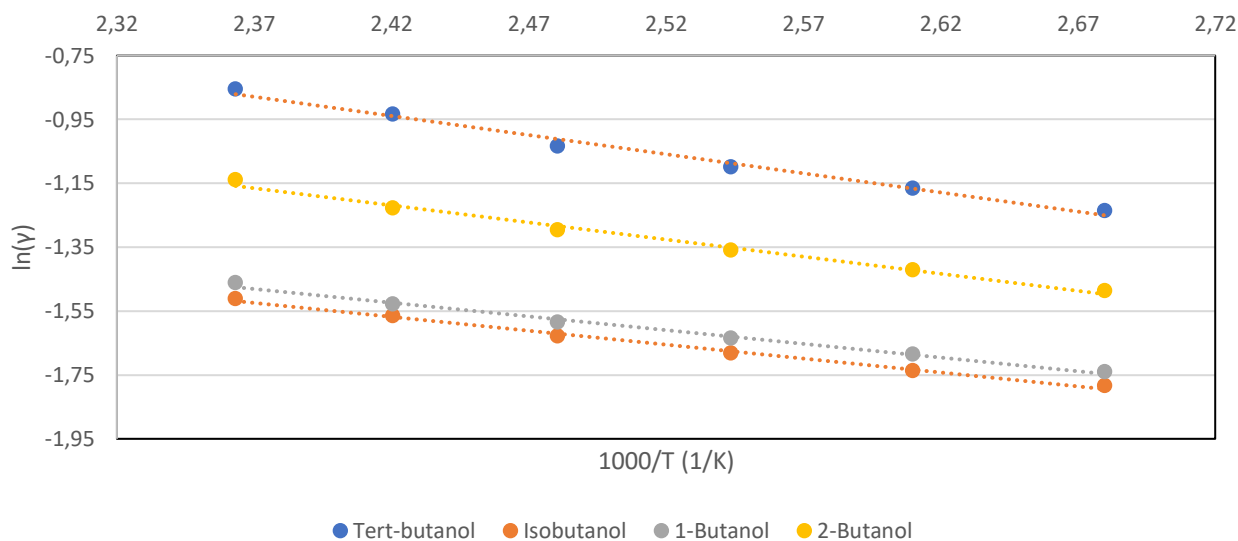
Figure 26 - $\ln(\gamma_{13}^{\infty})$ versus $1/T$ for several solutes in MIX[C_4mim][C_{12}mim]Cl. For tert-butanol, isobitanol, 1-butanol and 2-butanol.

Observing these figures, it can be seen that for the two ionic liquids the primary alcohols, isobutanol, and 1-butanol obtained values of $\ln(\gamma_{13}^{\infty})$ closer than the other solutes. If we compare the values of $\ln(\gamma_{13}^{\infty})$ in Figures 21 and 22 with those in Figures 23 and 24, the alcohol functional group itself already influences the value of $\ln(\gamma_{13}^{\infty})$ more than the position of the functional group, however, this also influences the value of $\ln(\gamma_{13}^{\infty})$. However, Figures 25 and 26 show a greater interaction for primary alcohols with the pure ionic liquids, whereas in secondary and tertiary alcohols it was possible to observe a greater interaction with the mixture of ionic liquids.

Now, the data of $\ln(\gamma_{13}^{\infty})$ for the terpenes and terpenoids will be presented. The data were obtained for six temperatures starting at 373.15 K and increasing by 10 K at a time. Figures 27 and 28 below show the values of $\ln(\gamma_{13}^{\infty})$ versus $1/T$ for α-pinene, β-pinene; p-cymene and R(+)-limonene.
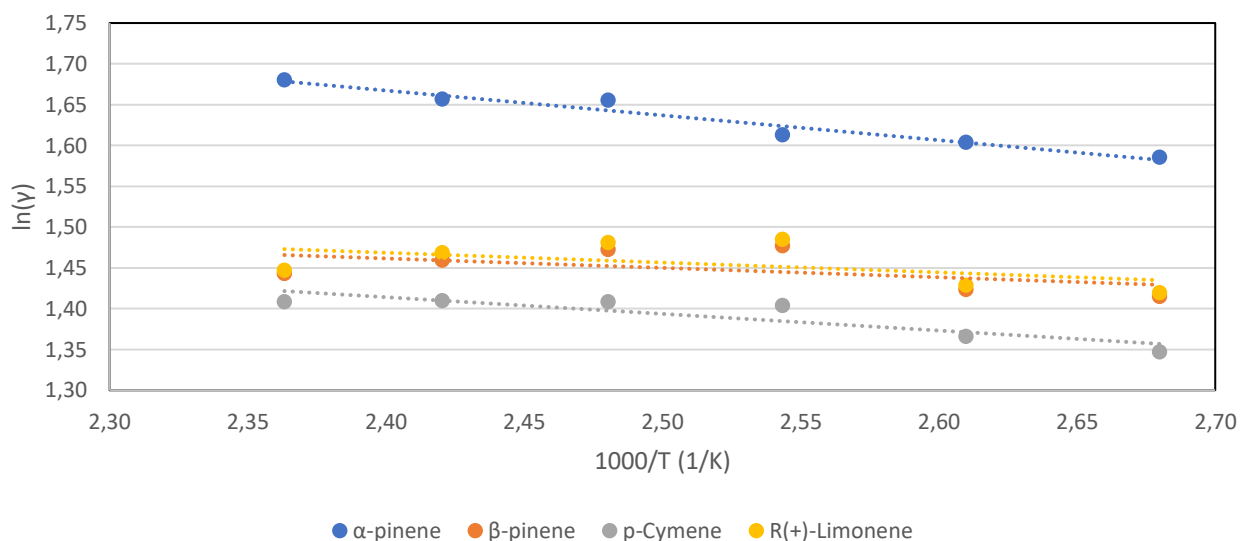
Figure 27 - ln (γ_{13}^{∞}) versus $1/T$ for several solutes in [C$_{12}$mim]Cl. For α-pinene, β-pinene, p-cymene and R(+)-limonene.
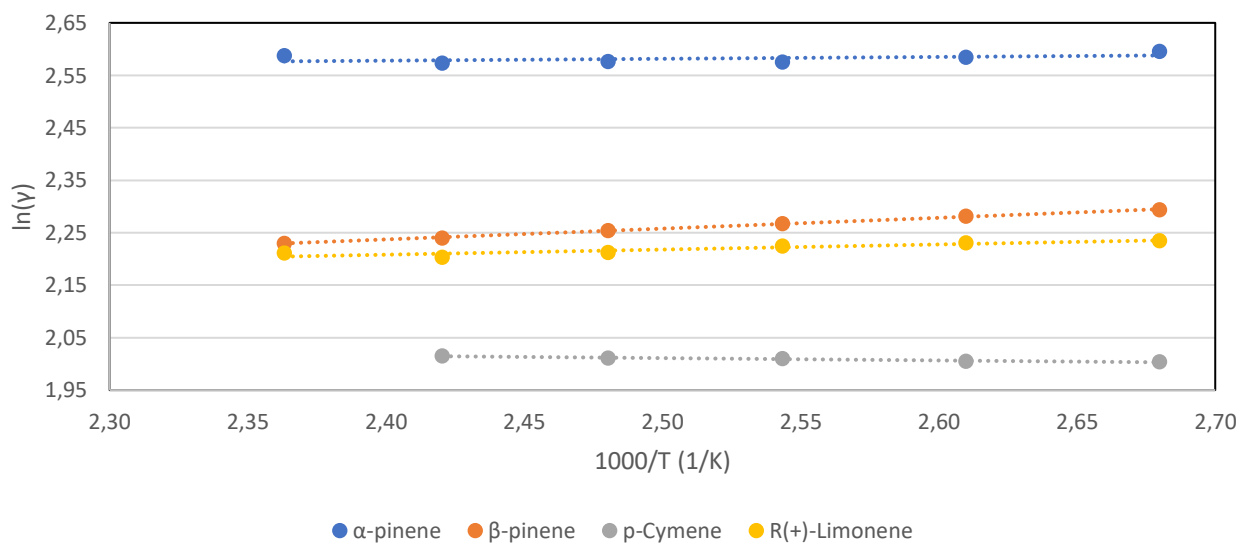
Figure 28 - ln(γ_{13}^{∞}) versus $1/T$ for several solutes in MIX[C$_4$mim][C$_{12}$mim]Cl. For α-pinene, β-pinene, p-cymene and R(+)-limonene.

For the two solvents, the values of ln(γ_{13}^{∞}) presented the same trend. α-pinene and β-pinene have a very similar molecular structure, but their ln(γ_{13}^{∞}) values were different, with β-pinene, show slightly better affinity indicating a greater interaction of β-pinene molecules with the ionic liquid. The pure ionic liquid presents stronger interactions for all solutes. Following, Figures 29 and 30 present the experimental data for α-pinene oxide and eucalyptol.
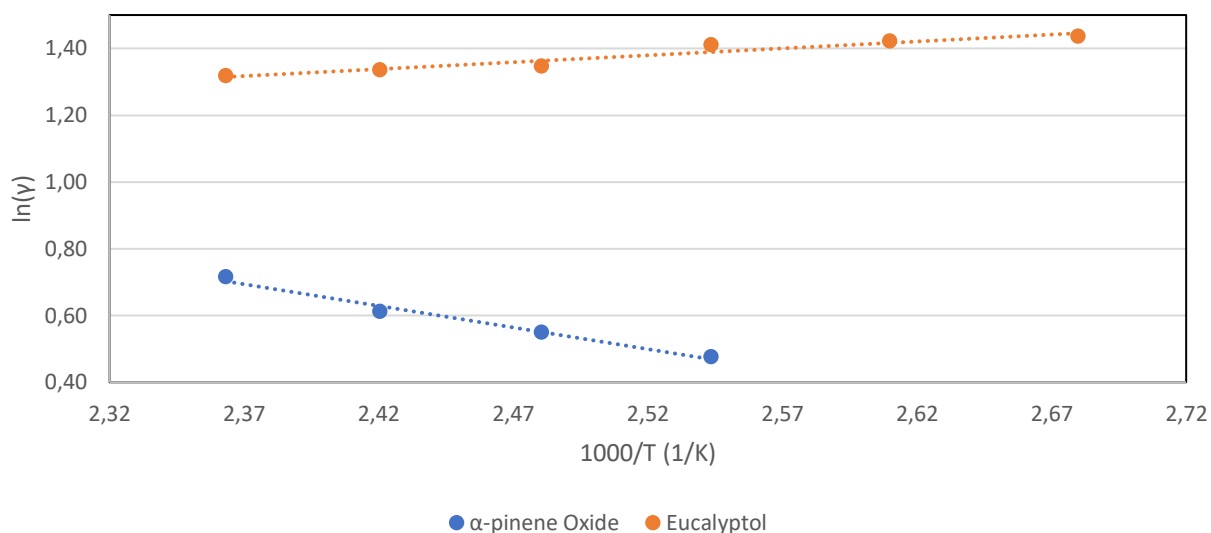
Figure 29 - $\ln(\gamma_{13}^{\infty})$ versus $1/T$ for several solutes in [C$_{12}$mim]Cl. For α-pinene oxide and eucalyptol.
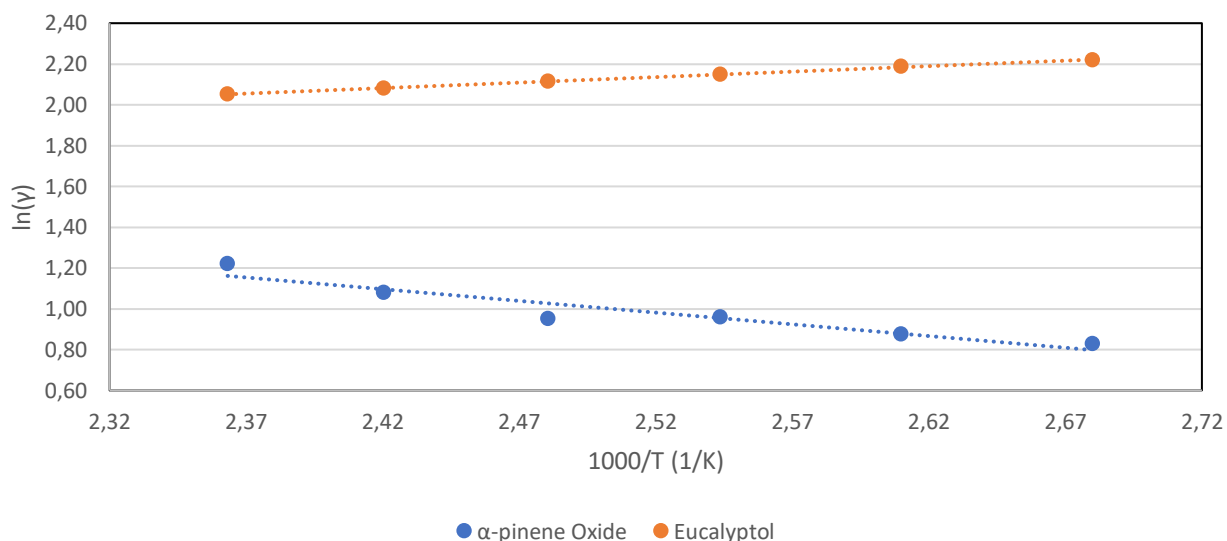
Figure 30 - $\ln(\gamma_{13}^{\infty})$ versus $1/T$ for several solutes in MIX[C$_4$mim][C$_{12}$mim]Cl. For α-pinene oxide and eucalyptol.

For these solutes above we can observe that the pure ionic liquid has a better interaction for α-pinene oxide and eucalyptol, and for these two solutes the molecular of α-pinene oxide interacted better with the ionic liquid. Figures 31 and 32 show the experimental data for the solutes, menthone, fenchone, γ-terpinene, and myrcene.
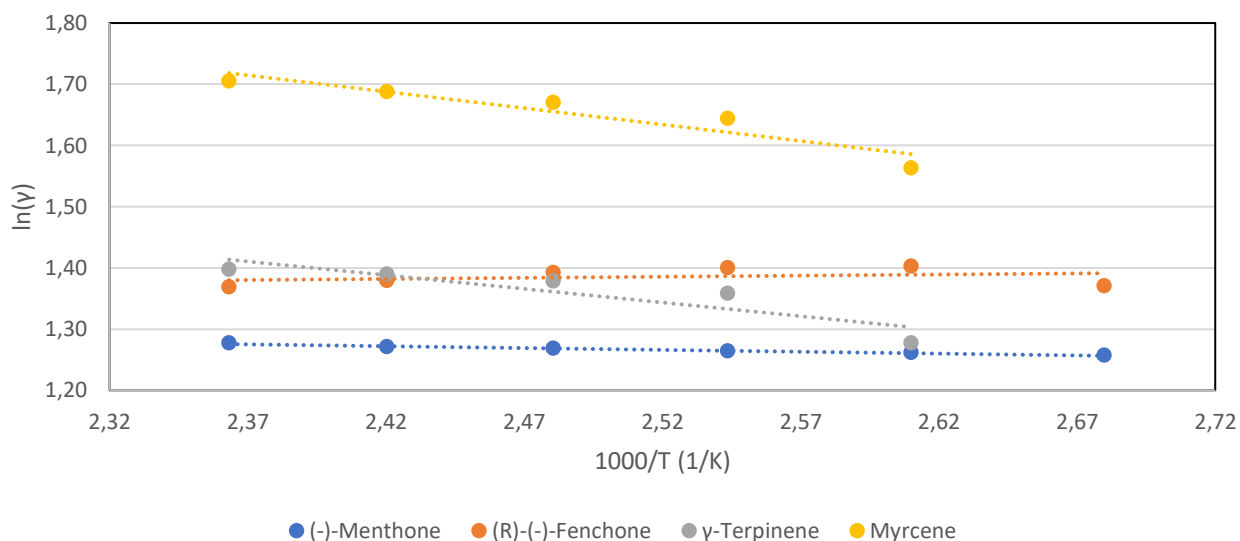
Figure 31 - $\ln(\gamma_{13}^{\infty})$ versus $1/T$ for several solutes in [C$_{12}$mim]Cl. For (-)-menthone, (R)-(-)-fenchone, γ-terpinene and myrcene.
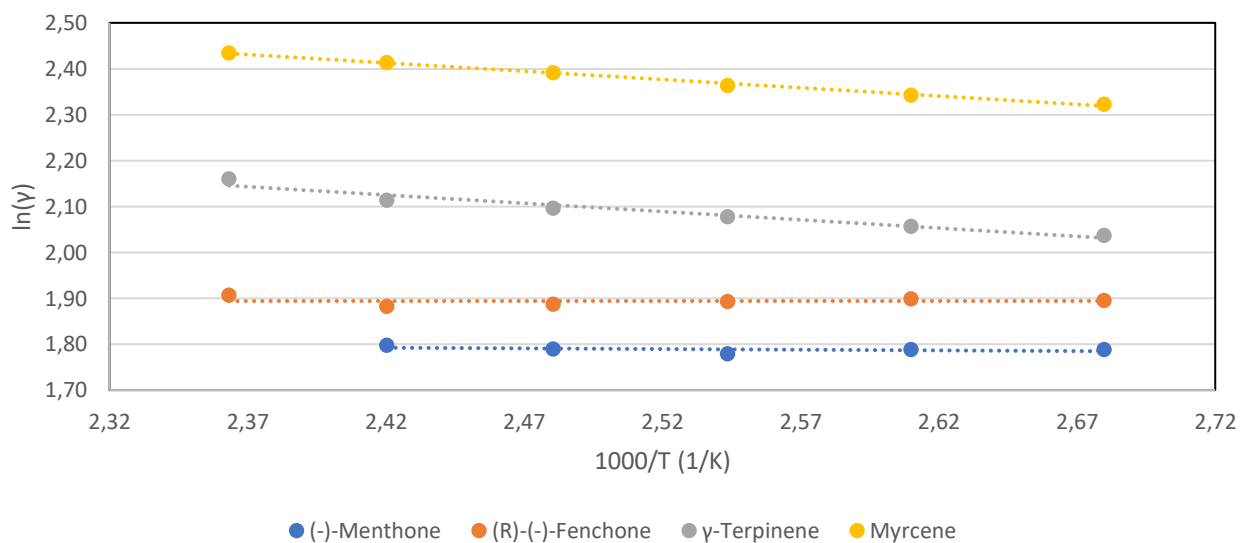
Figure 32 - $\ln(\gamma_{13}^{\infty})$ versus $1/T$ for several solutes in MIX[C$_4$mim][C$_{12}$mim]Cl. For (-)-menthone, (R)-(-)-fenchone, γ-terpinene and myrcene.

The experimental data for the solutes above were similar, showing a better interaction between the solutes and the pure ionic liquid. It was also possible to observe that the interaction between the pure ionic liquid and myrcene and γ-terpinene increases, with a decrease of temperature. Figures 33 and 34 show the data of $\ln(\gamma_{13}^{\infty})$ for water.
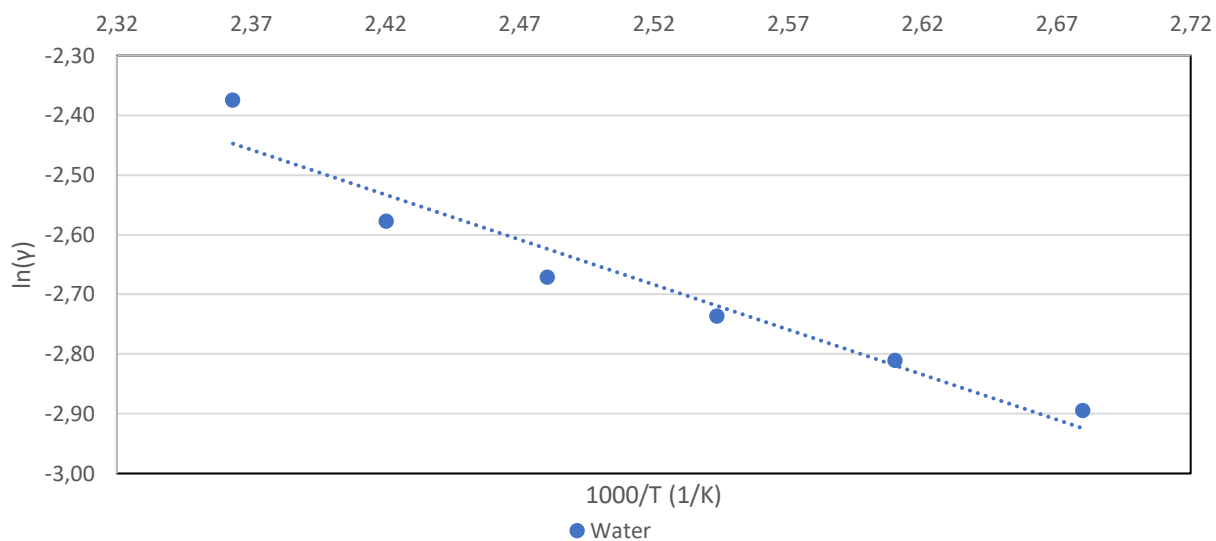
Figure 33 - $\ln(\gamma_{13}^\infty)$ versus $1/T$ for several solutes in [C$_{12}$mim]Cl. For water.
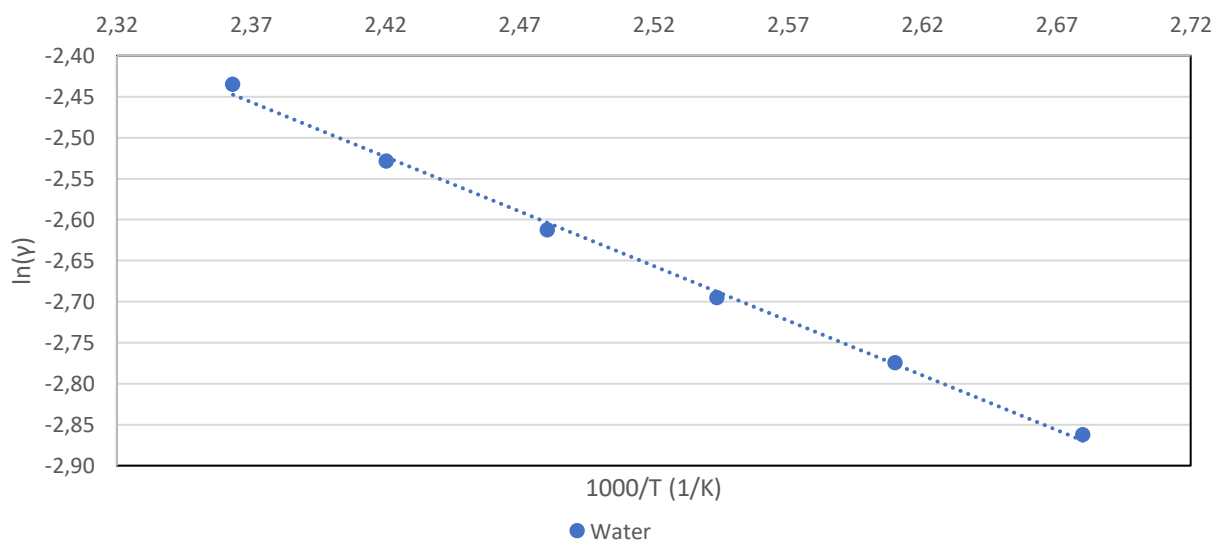
Figure 34 - $\ln(\gamma_{13}^\infty)$ versus $1/T$ for several solutes in MIX[C$_4$mim][C$_{12}$mim]Cl. For water.

Following the trend of terpenes, water has better interaction with the pure ionic liquid than the mixture of ionic liquids.
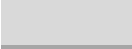
3.3.2 Selectivity and Capacity

One of the most significant objectives of this work is to explore the performance of ionic liquids in the fractionation of mixtures of terpenes. In that sense, the values of the selectivity (S_{ij}^∞)

and capacity (K_j^∞) are calculated to evaluate the performance of ionic liquids as solvents for those separations. The information obtained at the temperature of 383.15 K is presented in Figure 35.

For a solvent to be classified as suitable for the separation of terpenes, it must present high selectivity and capacity for the components to be separated (55). Using [C$_{12}$mim]Cl the selectivity in all possible separations is never higher than two and so this is not a good option. However, looking into the ionic liquid mixture results, all terpenes present a higher selectivity with α-pinene oxide, being quite promising in particular with α-pinene, myrcene, and β-pinene, and also very acceptable between α-pinene oxide and menthone.

Table 6 – Code of colors for selectivity and capacity.

Selectivity		Capacity	
	1 to 2		0.00 to 0.05
	2 to 4		0.05 to 0.10
	4 to 10		0.10 to 1.00
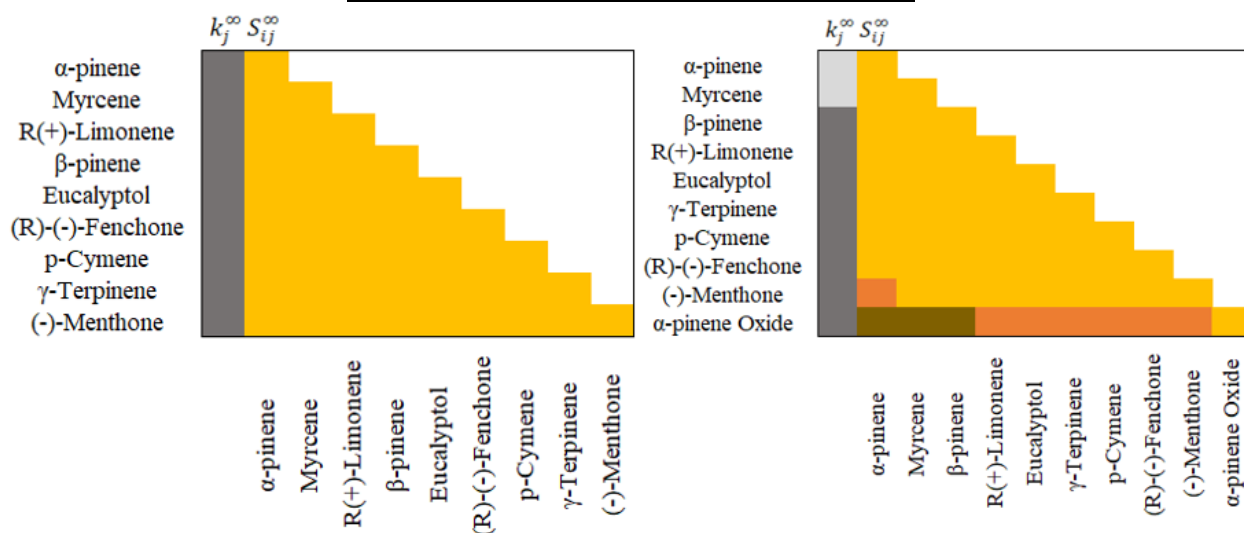
Figure 35 - Selectivity S_{ij}^∞ and capacity K_j^∞ for terpene separations at 383.15 K in [C$_{12}$mim]Cl in the left and MIX[C$_4$mim][C$_{12}$mim]Cl in the right. Table 6 shows the color scale.

In particular, for both hypothetical, moderate selectivity values were observed, for the important α-pinene/β-pinene separation; 1.20 (pure IL) while for the mixture of ionic liquids the

obtained selectivity was 1.35, while the capacities are 0.24 and 0.10, respectively, which are very disappointing. Using [C$_{12}$mim]Cl, the three highest selectivity values were obtained for the following separations: (−)-menthone/α-pinene, γ-terpinene/α-pinene, and for (−)-menthone/myrcene which are 1.41, 1.39, and 1.35, respectively. However, for the mixture of ionic liquids the three largest selectivity values were obtained for α-pinene oxide/α-pinene, α-pinene oxide/myrcene, and for α-pinene oxide/β-pinene with the values of 5.52, 4.34, and 4.08, respectively. The capacity values for these same separations for pure ionic liquid and the mixture were 0.241 and 1.020, respectively. All other separations present very small selectivities. For instance in the pure ionic liquids that parameter for eucalyptol/β-pinene, β-pinene/R(+)-limonene or eucalyptol/R(+)-limonene are, 1.002, 1.005 and 1.007, respectively, just showing the same affinity of these compound towards the ionic liquid, and turning impossible any feasible separation. For the mixture of ionic liquids values of that magnitude can also be found; eucalyptol/R(+)-limonene (1.043), R(+)-limonene/β-pinene (1.052), and p-cymene/γ-terpinene (1.054. If the separation between terpenes is expected to be very difficult, these results show that even between terpenes and their derived oxygenated molecules, the ILs cannot be very effective.

Table 7 shows values for selectivity and capacity for some separations, in the two pure ionic liquids, and their equimolar mixture. It is interesting to observe the consistency of the results where the selectivities in the mixture are always above, or below, the values of the pure compounds, suggesting some mixing effects and not just an ideal additivity rule, which can open new lines for future research.

Table 7 – Selectivity (S_{ij}^{∞}) and capacities (K_j^{∞}) for some separations at 383.15 K using different ILs.

Ionic liquids		[C$_4$mim]Cl[a]	Mix[C$_4$mim][C$_{12}$mim]Cl	[C$_{12}$mim]Cl
α-pinene/β-pinene	S_{ij}^{∞}	1.073	1.354	1.197
	K_j^{∞}	0.185	0.102	0.241
α-pinene/(−)-menthone	S_{ij}^{∞}	1.282	2.215	1.408
	K_j^{∞}	0.221	0.167	0.283
α-pinene/eucalyptol	S_{ij}^{∞}	1.128	1.486	1.199
	K_j^{∞}	0.194	0.112	0.241
α-pinene/α-pinene oxide	S_{ij}^{∞}	1.313	5.524	-
	K_j^{∞}	0.226	0.417	-
β-pinene/(1R)-(−)-fenchone	S_{ij}^{∞}	1.291	1.466	1.021
	K_j^{∞}	0.239	0.150	0.246
β-pinene/eucalyptol	S_{ij}^{∞}	1.052	1.098	1.002
	K_j^{∞}	0.194	0.112	0.241
Reference		(4)	This work	This work

(Solutes — row label spanning the left of the table)

[a] Interpolated value.

Chapter 4. Conclusion and future work

In this work, the potential of [C$_{12}$mim]Cl, and the equimolar mixture [C$_4$mim][C$_{12}$mim]Cl as separation agents was investigated through an experimental approach. The activity coefficients at infinite dilution and the gas-liquid partition coefficients were experimentally obtained for water, common organic solvents, and terpenes in these ionic liquids by gas-chromatography, in the temperature range (333.15 to 423.15) K. The differences between the coefficients and infinite dilution activity coefficients are very weak for terpenes and terpenoids, showing these ILs to have low potential as an agent for the purification of terpenic mixtures. Only for mixtures containing α-pinene oxide, some interesting selectivities were found but usually combined with low capacities. On the other hand, these preliminary results show that the combination of two ionic liquids can result in some interesting mixing effects inducing higher selectivities than those in the pure ILs. In this work, the anion was fixed, and just by changing the alkyl chain length of the imidazolium cation, some nice improvements were observed, notably for the separation between terpenes and ketone terpenoids, such as α-pinene/(−)-menthone or β-pinene/(1R)-(−)-fenchone. These results can open a new line of ideas about the combination of ionic liquids with anions presenting very different polarities, maintaining or not the cation.

An article with data from the work was published, indicating the relevance of the topic, for future work, it is relevant to evaluate the infinite dilution activity coefficients for the ionic liquid ([C8mim] Cl), to compare with the equimolar mixture of ionic liquids and ([C4mim] [C12mim] Cl), and assess whether the values are close to those measured for the mixture, as it has the same number of carbon molecules, but possibly a different structural network. It also biases the possibility of designing a mixture of ILs combining different characteristics of anions and cations, to obtain selectivities and features for a given separation problem, which should be the first screening using modeling approaches like COSMO-RS.

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Appendix A. Activity coefficients at infinite dilution

Table A.1 – Activity coefficients at infinite dilution for [C$_4$mim]Cl

Solutes	Temperature (K)									
	333,15	343,150	353,15	363,150	373,15	383,150	393,150	403,150	413,150	423,150
Heptane	5,942	6,153	5,957	6,109	6,350	6,219				
Octane	5,998	5,973	6,125	6,082	-	6,238				
Nonane	6,417	6,529	6,714	6,767	6,965	7,032				
Decane	7,355	7,382	7,490	7,521	7,784	7,698				
Cyclohexane	4,153	3,809	3,997	3,624	-	3,558				
Methylcyclohexane	4,168	4,035	4,092	4,095	4,248	4,117				
Benzene	1,214	1,243	1,264	1,287	1,302	1,320				
Toluene	1,466	1,504	1,556	1,585	1,696	1,634				
Ethylbenzene	1,844	1,925	1,935	2,000	2,104	2,096				
p-Xylene	1,875	1,942	1,988	2,037	2,128	2,161				
Methyl acetate	2,496	2,448	2,397	2,350	2,315	2,275				
Ethyl acetate	2,937	2,862	2,816	2,773	2,801	2,682				
Vinyl acetate	2,460	2,431	2,397	-	2,353	2,331				
THF	1,679	1,637	1,625	1,588	1,625	1,556				
1,4-dioxane	1,670	1,660	1,644	1,630	1,639	1,645				
Diethyl ether	4,797	4,646	4,481	4,585	4,405	4,072				
Acetonitrile	-	1,093	1,092	1,074	-	1,038				
Pyridine	-	-	-	1,040	1,015	0,998				
Thiophene	0,808	0,834	0,857	0,881	0,919	-				
Acetone	2,067	1,989	1,941	1,888	1,958	1,771				
2-Butanone	2,113	2,093	2,058	2,026	2,029	2,033				
Methanol					0,089	0,091	0,090	0,093	0,103	0,106
Ethanol					0,129	0,134	0,132	0,137	0,144	0,152
1-Propanol					0,131	-	0,140	0,148	0,157	0,168
2-Propanol					0,171	0,176	0,177	0,186	0,205	0,217
Isobutanol					0,131	0,139	0,143	0,152	0,162	0,175
1-Butanol					0,135	0,145	0,150	0,159	0,169	0,181
2-Butanol					0,179	0,191	0,196	0,210	0,226	0,245
Tert-butanol					0,232	0,252	-	0,274	0,297	0,320
Water					0,055	0,060	0,065	0,069	0,076	0,093
α-pinene					4,880	4,969	5,016	5,233	5,239	5,364
β-pinene					4,116	4,151	4,377	4,358	4,302	4,233
R(+)-Limonene					4,134	4,171	4,414	4,396	4,341	4,249
p-Cymene					3,844	3,918	4,070	4,089	4,094	4,089
γ-Terpinene					-	3,585	3,887	3,967	4,011	4,044

Myrcene	-	4,774	5,173	5,311	5,404	5,502
(-)-Menthone	3,513	3,530	3,540	3,553	3,565	3,585
(R)-(-)-Fenchone	3,937	4,064	4,056	4,023	3,971	3,929
α-pinene Oxide	-	-	1,609	1,731	1,842	2,044
Eucalyptol	4,205	4,144	4,098	3,844	3,798	3,735

Table A.2 – Activity coefficients at infinite dilution for [C$_4$mim][C$_{12}$mim]Cl

Solutes	Temperature (K)									
	333.15	343.150	353.15	363.150	373.15	383.150	393.150	403.150	413.150	423.150
Heptane	30.188	28.366	27.190	25.650	24.679	23.763				
Octane	26.017	24.916	24.099	23.008	23.011	22.606				
Nonane	24.134	23.821	23.523	23.225	22.933	22.487				
Decane	27.307	27.718	27.561	26.726	27.708	26.946				
Cyclohexane	20.597	17.415	15.522	13.793	12.602	11.858				
Methylcyclohexane	19.542	17.252	15.533	14.472	13.565	12.912				
Benzene	1.992	1.952	1.960	1.928	1.945	1.924				
Toluene	2.611	2.624	2.643	2.638	2.658	2.648				
Ethylbenzene	3.501	3.490	3.505	3.505	3.511	3.513				
p-Xylene	3.554	3.564	3.596	3.597	3.616	3.622				
Methyl acetate	3.370	3.208	3.064	2.984	2.897	2.852				
Ethyl acetate	4.589	4.346	4.196	4.080	3.990	3.820				
Vynyl acetate	3.333	3.213	3.123	3.059	3.032	2.974				
THF	2.836	2.667	2.603	2.516	2.423	2.393				
1,4-dioxane	2.089	2.050	2.031	1.999	1.971	1.934				
Diethyl ether	15.023	13.623	12.168	11.157	10.250	9.900				
Acetonitrile	0.977	0.974	0.977	0.974	0.974	0.971				
Pyridine	1.123	1.120	1.118	1.109	1.105	1.104				
Thiophene	1.086	1.104	1.126	1.140	1.161	1.181				
Acetone	2.443	2.303	2.214	2.148	2.072	1.992				
2-Butanone	2.739	2.634	2.553	2.507	2.454	2.431				
Methanol					0.089	0.093	0.097	0.101	0.105	0.111
Ethanol					0.140	0.145	0.151	0.158	0.164	0.173
1-Propanol					0.155	0.163	0.172	0.180	0.191	0.203
2-Propanol					0.204	0.214	0.225	0.236	0.249	0.267
Isobutanol					0.168	0.176	0.186	0.196	0.209	0.220
1-Butanol					0.175	0.185	0.195	0.205	0.217	0.232
2-Butanol					0.226	0.241	0.257	0.273	0.293	0.320
Tert-butanol					0.290	0.312	0.333	0.356	0.393	0.425
Water					0.057	0.062	0.068	0.073	0.080	0.088

α-pinene	13.408	13.249	13.140	13.150	13.105	13.297
β-pinene	9.913	9.789	9.655	9.531	9.392	9.300
R(+)-Limonene	9.349	9.302	9.251	9.140	9.053	9.124
p-Cymene	7.416	7.425	7.463	7.473	7.500	-
γ-Terpinene	7.667	7.823	7.988	8.139	8.280	8.669
Myrcene	10.199	10.412	10.624	10.932	11.176	11.408
(-)-Menthone	5.979	5.980	5.925	5.989	6.034	-
(R)-(-)-Fenchone	6.656	6.677	6.642	6.602	6.572	6.731
α-pinene Oxide	2.290	2.398	2.608	2.591	2.947	3.387
Eucalyptol	9.195	8.917	8.567	8.289	8.009	7.780

Table A3. Value of $\ln(\gamma_{13}^{\infty})$ for all solutes in [C4mim]Cl.

Solutes	Temperature (K)									
	333.15	343.150	353.15	363.150	373.15	383.150	393.150	403.150	413.150	423.150
Heptane	1.782	1.817	1.785	1.810	1.848	1.828				
Octane	1.791	1.787	1.812	1.805	-	1.831				
Nonane	1.859	1.876	1.904	1.912	1.941	1.950				
Decane	1.995	1.999	2.014	2.018	2.052	2.041				
Cyclohexane	1.424	1.337	1.386	1.288	-	1.269				
Methylcyclohexane	1.427	1.395	1.409	1.410	1.446	1.415				
Benzene	0.194	0.218	0.234	0.252	0.264	0.277				
Toluene	0.383	0.408	0.442	0.461	0.528	0.491				
Ethylbenzene	0.612	0.655	0.660	0.693	0.744	0.740				
p-Xylene	0.629	0.664	0.687	0.711	0.755	0.770				
Methyl acetate	0.915	0.895	0.874	0.854	0.839	0.822				
Ethyl acetate	1.078	1.052	1.035	1.020	1.030	0.987				
Vynyl acetate	0.900	0.888	0.874		0.856	0.846				
THF	0.518	0.493	0.486	0.463	0.486	0.442				
1,4-dioxane	0.513	0.507	0.497	0.489	0.494	0.498				
Diethyl ether	1.568	1.536	1.500	1.523	1.483	1.404				
Acetonitrile	-	0.089	0.088	0.072	-	0.037				
Pyridine	-	-	-	0.039	0.015	-0.002				
Thiophene	-0.213	-0.182	-0.155	-0.127	-0.084	-				
Acetone	0.726	0.688	0.663	0.636	-	0.572				
2-Butanone	0.748	0.739	0.722	0.706	0.708	0.710				
Methanol					-2.418	-2.400	-2.410	-2.374	-2.271	-2.242
Ethanol					-2.049	-2.012	-2.024	-1.985	-1.936	-1.887
1-Propanol					-2.034	-	-1.967	-1.908	-1.851	-1.783
2-Propanol					-1.765	-1.736	-1.729	-1.681	-1.583	-1.527

Solutes						
Isobutanol	-2.033	-1.971	-1.945	-1.885	-1.820	-1.746
1-Butanol	-2.000	-1.929	-1.899	-1.841	-1.778	-1.708
2-Butanol	-1.719	-1.653	-1.629	-1.559	-1.488	-1.408
Tert-butanol	-1.460	-1.379	-	-1.295	-1.213	-1.140
Water	-2.895	-2.811	-2.737	-2.672	-2.578	-2.375
α-pinene	1.585	1.603	1.613	1.655	1.656	1.680
β-pinene	1.415	1.423	1.476	1.472	1.459	1.443
R(+)-Limonene	1.419	1.428	1.485	1.481	1.468	1.447
p-Cymene	1.347	1.366	1.404	1.408	1.410	1.408
γ-Terpinene	-	1.277	1.358	1.378	1.389	1.397
Myrcene	-	1.563	1.643	1.670	1.687	1.705
(-)-Menthone	1.257	1.261	1.264	1.268	1.271	1.277
(R)-(-)-Fenchone	1.371	1.402	1.400	1.392	1.379	1.368
α-pinene Oxide	-	-	0.475	0.549	0.611	0.715
Eucalyptol	1.436	1.422	1.410	1.346	1.334	1.318

Table A4. Value of $\ln(\gamma_{13}^{\infty})$ for all solutes in [C$_4$mim][C$_{12}$mim]Cl.

Solutes	Temperature (K)									
	333.15	343.150	353.15	363.150	373.15	383.150	393.150	403.150	413.150	423.150
Heptane	3.407	3.345	3.303	3.245	3.206	3.168				
Octane	3.259	3.216	3.182	3.136	3.136	3.118				
Nonane	3.184	3.171	3.158	3.145	3.133	3.113				
Decane	3.307	3.322	3.316	3.286	3.322	3.294				
Cyclohexane	3.025	2.857	2.742	2.624	2.534	2.473				
Methylcyclohexane	2.973	2.848	2.743	2.672	2.607	2.558				
Benzene	0.689	0.669	0.673	0.656	0.665	0.654				
Toluene	0.960	0.965	0.972	0.970	0.978	0.974				
Ethylbenzene	1.253	1.250	1.254	1.254	1.256	1.257				
p-Xylene	1.268	1.271	1.280	1.280	1.285	1.287				
Methyl acetate	1.215	1.166	1.120	1.093	1.064	1.048				
Ethyl acetate	1.524	1.469	1.434	1.406	1.384	1.340				
Vynyl acetate	1.204	1.167	1.139	1.118	1.109	1.090				
THF	1.043	0.981	0.957	0.923	0.885	0.872				
1,4-dioxane	0.737	0.718	0.709	0.693	0.678	0.660				
Diethyl ether	2.710	2.612	2.499	2.412	2.327	2.293				
Acetonitrile	-0.023	-0.026	-0.024	-0.026	-0.026	-0.030				
Pyridine	0.116	0.113	0.111	0.103	0.100	0.099				
Thiophene	0.082	0.099	0.119	0.131	0.150	0.166				
Acetone	0.893	0.834	0.795	0.765	0.729	0.689				

2-Butanone	1.008	0.969	0.937	0.919	0.898	0.888				
Methanol					-2.423	-2.377	-2.336	-2.294	-2.250	-2.196
Ethanol					-1.963	-1.928	-1.888	-1.848	-1.805	-1.755
1-Propanol					-1.864	-1.813	-1.763	-1.715	-1.657	-1.593
2-Propanol					-1.588	-1.542	-1.492	-1.444	-1.392	-1.319
Isobutanol					-1.785	-1.738	-1.682	-1.629	-1.565	-1.512
1-Butanol					-1.740	-1.685	-1.636	-1.585	-1.529	-1.462
2-Butanol					-1.486	-1.422	-1.360	-1.296	-1.228	-1.139
Tert-butanol					-1.236	-1.166	-1.099	-1.034	-0.934	-0.856
Water					-2.863	-2.775	-2.695	-2.612	-2.529	-2.435
α-pinene					2.596	2.584	2.576	2.576	2.573	2.588
β-pinene					2.294	2.281	2.268	2.255	2.240	2.230
R(+)-Limonene					2.235	2.230	2.225	2.213	2.203	2.211
p-Cymene					2.004	2.005	2.010	2.011	2.015	
γ-Terpinene					2.037	2.057	2.078	2.097	2.114	2.160
Myrcene					2.322	2.343	2.363	2.392	2.414	2.434
(-)-Menthone					1.788	1.788	1.779	1.790	1.797	
(R)-(-)-Fenchone					1.896	1.899	1.893	1.887	1.883	1.907
α-pinene Oxide					0.829	0.875	0.959	0.952	1.081	1.220
Eucalyptol					2.219	2.188	2.148	2.115	2.081	2.052

Table A5. Capacities for all solutes in [C$_4$mim]Cl.

Solutes	Temperature (K)									
	333.15	343.150	353.15	363.150	373.15	383.150	393.150	403.150	413.150	423.150
Heptane	0.168	0.163	0.168	0.164	0.157	0.161				
Octane	0.167	0.167	0.163	0.164	-	0.160				
Nonane	0.156	0.153	0.149	0.148	0.144	0.142				
Decane	0.136	0.135	0.134	0.133	0.128	0.130				
Cyclohexane	0.241	0.263	0.250	0.276	-	0.281				
Methylcyclohexane	0.240	0.248	0.244	0.244	0.235	0.243				
Benzene	0.824	0.804	0.791	0.777	0.768	0.758				
Toluene	0.682	0.665	0.643	0.631	0.590	0.612				
Ethylbenzene	0.542	0.520	0.517	0.500	0.475	0.477				
p-Xylene	0.533	0.515	0.503	0.491	0.470	0.463				
Methyl acetate	0.401	0.409	0.417	0.426	0.432	0.440				
Ethyl acetate	0.340	0.349	0.355	0.361	0.357	0.373				
Vynyl acetate	0.406	0.411	0.417		0.425	0.429				
THF	0.596	0.611	0.615	0.630	0.615	0.643				
1,4-dioxane	0.599	0.603	0.608	0.613	0.610	0.608				

Solutes	333.15	343.150	353.15	363.150	373.15	383.150	393.150	403.150	413.150	423.150
Diethyl ether	0.208	0.215	0.223	0.218	0.227	0.246				
Acetonitrile	-	0.915	0.916	0.931	-	0.963				
Pyridine	-	-	-	0.961	0.985	1.002				
Thiophene	1.238	1.199	1.167	1.135	1.088	-				
Acetone	0.484	0.503	0.515	0.530	0.511	0.565				
2-Butanone	0.473	0.478	0.486	0.493	0.493	0.492				
Methanol					11.226	11.025	11.139	10.743	9.688	9.413
Ethanol					7.758	7.481	7.570	7.281	6.933	6.597
1-Propanol					7.641	-	7.146	6.743	6.368	5.950
2-Propanol					5.840	5.676	5.637	5.373	4.870	4.602
Isobutanol					7.635	7.179	6.996	6.586	6.171	5.730
1-Butanol					7.388	6.880	6.682	6.300	5.917	5.516
2-Butanol					5.578	5.225	5.100	4.754	4.427	4.089
Tert-butanol					4.306	3.969	-	3.649	3.363	3.126
Water					18.081	16.627	15.437	14.471	13.169	10.753
α-pinene					0.205	0.201	0.199	0.191	0.191	0.186
β-pinene					0.243	0.241	0.228	0.229	0.232	0.236
R(+)-Limonene					0.242	0.240	0.227	0.227	0.230	0.235
p-Cymene					0.260	0.255	0.246	0.245	0.244	0.245
γ-Terpinene					-	0.279	0.257	0.252	0.249	0.247
Myrcene					-	0.209	0.193	0.188	0.185	0.182
(-)-Menthone					0.285	0.283	0.283	0.281	0.281	0.279
(R)-(-)-Fenchone					0.254	0.246	0.247	0.249	0.252	0.255
α-pinene Oxide					-	-	0.622	0.578	0.543	0.489
Eucalyptol					0.238	0.241	0.244	0.260	0.263	0.268
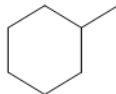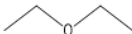
Table A6. Capacities for all solutes in [C$_4$mim][C$_{12}$mim]Cl.
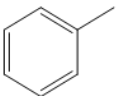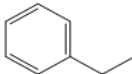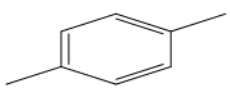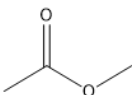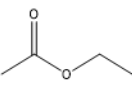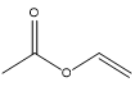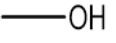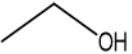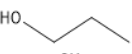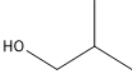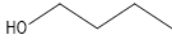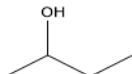
Solutes	Temperature (K)									
	333.15	343.150	353.15	363.150	373.15	383.150	393.150	403.150	413.150	423.150
Heptane	0.033	0.035	0.037	0.039	0.041	0.042				
Octane	0.038	0.040	0.041	0.043	0.043	0.044				
Nonane	0.041	0.042	0.043	0.043	0.044	0.044				
Decane	0.037	0.036	0.036	0.037	0.036	0.037				
Cyclohexane	0.049	0.057	0.064	0.073	0.079	0.084				
Methylcyclohexane	0.051	0.058	0.064	0.069	0.074	0.077				
Benzene	0.502	0.512	0.510	0.519	0.514	0.520				
Toluene	0.383	0.381	0.378	0.379	0.376	0.378				
Ethylbenzene	0.286	0.287	0.285	0.285	0.285	0.285				
p-Xylene	0.281	0.281	0.278	0.278	0.277	0.276				
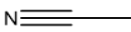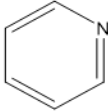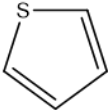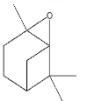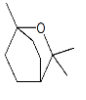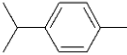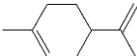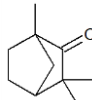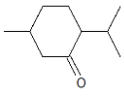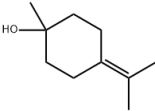
Methyl acetate	0.297	0.312	0.326	0.335	0.345	0.351						
Ethyl acetate	0.218	0.230	0.238	0.245	0.251	0.262						
Vynyl acetate	0.300	0.311	0.320	0.327	0.330	0.336						
THF	0.353	0.375	0.384	0.398	0.413	0.418						
1,4-dioxane	0.479	0.488	0.492	0.500	0.507	0.517						
Diethyl ether	0.067	0.073	0.082	0.090	0.098	0.101						
Acetonitrile	1.023	1.026	1.024	1.027	1.026	1.030						
Pyridine	0.891	0.893	0.895	0.902	0.905	0.906						
Thiophene	0.921	0.906	0.888	0.877	0.861	0.847						
Acetone	0.409	0.434	0.452	0.465	0.483	0.502						
2-Butanone	0.365	0.380	0.392	0.399	0.407	0.411						
Methanol							11.284	10.770	10.336	9.918	9.492	8.986
Ethanol							7.124	6.878	6.603	6.349	6.081	5.783
1-Propanol							6.451	6.129	5.830	5.559	5.245	4.920
2-Propanol							4.894	4.672	4.448	4.237	4.021	3.739
Isobutanol							5.958	5.687	5.378	5.096	4.784	4.537
1-Butanol							5.698	5.393	5.136	4.881	4.614	4.316
2-Butanol							4.420	4.146	3.897	3.656	3.415	3.125
Tert-butanol							3.443	3.210	3.002	2.811	2.545	2.354
Water							17.507	16.034	14.812	13.632	12.535	11.421
α-pinene							0.075	0.075	0.076	0.076	0.076	0.075
β-pinene							0.101	0.102	0.104	0.105	0.106	0.108
R(+)-Limonene							0.107	0.108	0.108	0.109	0.110	0.110
p-Cymene							0.135	0.135	0.134	0.134	0.133	-
γ-Terpinene							0.130	0.128	0.125	0.123	0.121	0.115
Myrcene							0.098	0.096	0.094	0.091	0.089	0.088
(-)-Menthone							0.167	0.167	0.169	0.167	0.166	-
(R)-(-)-Fenchone							0.150	0.150	0.151	0.151	0.152	0.149
α-pinene Oxide							0.437	0.417	0.383	0.386	0.339	0.295
Eucalyptol							0.109	0.112	0.117	0.121	0.125	0.129

Appendix B. List of solutes

Table B.1 – Names, sources and mass fraction purities of the organic solutes used. Names in parentheses correspond to common names used in the text.

	Chemicals		Source	Mass fraction puritya
Alkanes	Heptane		Aldrich	≥ 0.990
	Octane		Aldrich	≥ 0.990
	Nonane		Aldrich	≥ 0.990
	Decane		Aldrich	≥ 0.990
Cycloalkanes	Cyclohexane		Aldrich	≥ 0.990
	Methylcyclohexane		Aldrich	≥ 0.990
Ketones	Propan-2-one (Acetone)		Aldrich	≥ 0.990
	Butan-2-one		VWR Chemicals	0.999
Ethers	Ethoxyethane (Diethyl ether)		Aldrich	≥ 0.999
Cyclic Ethers	Oxolane (THF)		Aldrich	≥ 0.999
	1,4-Dioxane		Aldrich	≥ 0.998

Aromatic Hydrocarbons	Benzene		Aldrich	≥ 0.998
	Toluene		Aldrich	≥ 0.998
	Ethylbenzene		Aldrich	≥ 0.998
	p-Xylene		Aldrich	≥ 0.990
Esters	Methyl acetate		Aldrich	≥ 0.998
	Ethyl acetate		Aldrich	≥ 0.998
	Vinyl acetate		Aldrich	≥ 0.990
Alcohols	Methanol	—OH	Aldrich	≥ 0.999
	Ethanol		Aldrich	≥ 0.998
	Propan-1-ol		Aldrich	≥ 0.999
	Propan-2-ol		Fluka	≥ 0.999
	2-Methyl-propan-1-ol (Isobutanol)		Aldrich	≥ 0.995
	Butan-1-ol		Aldrich	≥ 0.998
	Butan-2-ol		Aldrich	≥ 0.995
	2-Methyl-propan-2-ol (*tert*-Butanol)		Aldrich	≥ 0.997

		OH		
		(structure: t-butanol)		
	Acetonitrile	N≡	Fluka	≥ 0.999
	Pyridine	(pyridine structure)	Aldrich	≥ 0.998
	Thiophene	(thiophene structure)	Aldrich	≥ 0.990
	Water	H_2O		
	α-Pinene	(α-pinene structure)	Sigma-Aldrich	0.980
	β-Pinene	(β-pinene structure)	Sigma-Aldrich	0.990
	α-Pinene Oxide	(α-pinene oxide structure)	Aldrich	0.970
Terpenes/ Terpenoids	Eucalyptol	(eucalyptol structure)	Aldrich	0.990
	P-Cymmene	(p-cymene structure)	Aldrich	0.990
	(R)-(+)-Limonene	(limonene structure)	Aldrich	0.970
	(R)-(-)-Fenchone	(fenchone structure)	Aldrich	≥ 0.980
	(-)-Menthone	(menthone structure)	Fluka	≥ 0.990
	γ-Terpinene	(structure)	Aldrich	0.990

Myrcene		Aldrich	0.990