

Ionic liquids in the fractionation of terpenes and other relevant separation problems

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“Por vezes sentimos que aquilo que fazemos não é senão uma gota de água no mar.

Mas o mar seria menor se lhe faltasse uma gota”

Madre Teresa de Calcutá

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Abstract

Terpenes include a great variety of compounds with different functions, some acting as flavoring or aroma agents, or organic solvents, while others can be used as raw material for the synthesis of other compounds of commercial interest in different industrial areas. With an increase in environmental concern, some terpenes can represent greener options for industrial processes, increasing the interest of the scientific community on its properties and behavior. In order to purify those compounds and their mixtures, and therefore increase their value, various methods are applied. Among those methods, vacuum distillation has been widely applied. Furthermore, studies associating with ionic liquids (ILs) as separation agents in deterpenation processes hold economical and environment appeal. In the present work, infinite dilution activity coefficient data of several organic solutes (alkanes, cycloalkanes, ketones, ethers, cycloethers, aromatic hydrocarbons, esters, acetonitrile, pyridine, thiophene, alcohols, terpenes and terpenoids) and water in selected ionic liquids ($[P_{6,6,6,14}][(C_8H_{17})_2PO_2]$ or $[P_{6,6,6,14}][Cl]$) were obtained by gas-liquid chromatography (GLC), aiming to estimate selectivities and capacities values related to different separation problems including those involving terpenes mixtures. Both ILs tested showed poor entrainment potential regarding the α -pinene/ β -pinene separation, while $[P_{6,6,6,14}][(C_8H_{17})_2PO_2]$ showed potential as an entrainer in the limonene/linalool separation. The partial excess energies of alcoholic solutes showed the most distinct behavior from all solutes in both ILs, indicating to be mostly governed by enthalpic interactions.

Keywords: Gas-Liquid Chromatography; Deterpenation; Ionic Liquid; Selectivity, Capacity

Resumo

Terpenos abrangem uma grande variedade de compostos com funções distintas, alguns agindo como agentes de sabor e aroma, ou solventes orgânicos, enquanto outros podem ser usados como matéria-prima para sínteses de compostos de interesse comercial no âmbito industrial. Com o aumento da consciência ambiental, terpenos representam opções mais verdes para processos industriais, tendo aumentando enormemente o interesse da comunidade científica nas suas propriedades e comportamentos. Para purificar esses compostos e suas misturas, adicionando-lhe valor, vários métodos são aplicados. Dentre esses métodos, destilação a vácuo tem sido amplamente aplicado. Além disso, estudos associando líquidos iônicos (LIs) como agentes de separação em desterpanações carrega apelo econômico e ambiental. No presente trabalho, coeficientes de atividade a diluição infinita de vários solventes orgânicos (alcanos, ciclo alcanos, cetonas, éteres, ciclo éteres, hidrocarbonetos aromáticos, ésteres, acetonitrilo, piridina, terpenos e terpenóides) e água em líquidos iônicos ($[P_{6,6,6,14}][(C_8H_{17})_2PO_2]$ ou $[P_{6,6,6,14}][Cl]$) são obtidos por meio de cromatografia gás-líquido, almejando estimar valores de seletividades e capacidades relacionados a diferentes separações comuns, bem como aquelas contendo misturas de terpenos. Ambos LIs testados mostraram pouco potencial como facilitadores da separação α -pineno/ β -pineno, enquanto $[P_{6,6,6,14}][(C_8H_{17})_2PO_2]$ mostrou potencial como facilitador da separação limoneno/linalol. As energias parciais em excesso dos solutos alcoólicos mostraram o comportamento mais distintos entre todos os solutos, com tipo de interação de dominância entálpica.

Palavras-Chave: Cromatografia gás-líquido; Desterpanação; Líquidos Iônicos; Seletividade, Capacidade.

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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
K_L	Gas-Liquid Partition Coefficient
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 de oven of the Gas-Chromatographer
P_a^*	Vapor Pressure of pure compound a

Greek Letters

γ_{ab}^∞	Activity Coefficient at Infinite Dilution of compound b in LI
ρ_a	Density of compound a

List of Acronyms

COSMO-RS	Conductor-like Screening Model for Real Solvents
DES	Deep Eutectic Solvents
GLC	Gas-Liquid Chromatography
IDAC	Infinite Dilution Activity Coefficient

IL	Ionic Liquids
LLE	Liquid-Liquid Equilibria
RTIL	Room Temperature Ionic Liquids

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Chapter 1. Introduction

1.1. Importance and objectives

Environmental awareness is an important factor to consider whenever a product or process is being created or improved, at least as important as the economic factors or efficiency. All industrial areas are affected by these concerns and separation processes are no exception, requiring to be designed applying greener technologies and compounds.

Some mixtures challenge even the most efficient separation processes, requiring large amounts of energy, time, and so, investment. Some essential oils certainly fall in this category of “defiant” mixtures due to their main compounds: terpenes and terpenoids. In order to exemplify the relevance of essential oils and its compounds, turpentine, the most produced essential oil in the world, boasts an annual production of around 330,000 tons. Additionally, the two main constituents of this essential oil are terpenes (α -pinene and β -pinene), which have an annual production of 30,000 tons [1] and each one has its own application fields.

Separation agents are often used in difficult separation processes in order to achieve better cost-efficiency parameters. However, maintaining the process efficient and greener is not a simple task. Some good candidates for this job are ionic liquids (IL), with some exceptions regarding environmental concerns. Chronologically, the first IL reported dates to mid-1910s, however, they were air- and water-sensitives. Air- and water-stable ILs were studied in early-1990s and bio-renewable ones, around 2000s [2]. Although being widely studied only after the early-2000s, many studies were made testing different IL in various separation processes [3–7], including those applied to essential oils mixtures [1,8–12].

The present work aims to contribute to the development of novel approaches to the fractionation and purification of terpenes using ILs as extraction agents, in liquid-liquid extraction or distillation processes. Initially, ILs with polar anions and non-polar cations, like alkyl ammonium or phosphonium, will be studied, evaluating their capabilities to fractionate essential oils rich in terpenes, such as pinenes, limonene, linalool, citronellol and geraniol. The selection of these compounds reflects their industrial relevance and significant presence in various essential oils, as well as functional variety, contributing also with to the goal of deterpenation.

Thus, the main objectives of the thesis work are:

1 – Measurement, by gas-liquid chromatography, of the activity coefficients at infinite dilution of water and organic solutes (including terpenes) in ionic liquids.

2 – Analysis of the selectivity and capacity of the ionic liquids, containing phosphonium cations, having in view the fractionation of terpenes and other relevant separation problems.

To support the above objectives, the present work includes an introduction detailing the importance of terpenes in a broader view, industrial processes to separate them, commercially interesting mixtures and potential separation agents to ease those separations (ionic liquids or deep eutectic solvents)

1.2. Content

Chapter 2 consists of a literature review about the subjects studied in the present work. It starts with a description and characterization of the terpenes and terpenoids and their usage in ancient and modern society, along with the common methods to separate them from the natural matrices in which they are found. It follows with the description of ionic liquids and deep eutectic solvents, as well as previous works that use both of those compounds/mixtures as entrainers to facilitate the separation processes of terpenes and terpenoids. It finishes specifying the method used in the present work, gas-liquid chromatography (GLC). Alongside, it also shows the necessary equations to calculate the physicochemical properties, activity coefficient at infinite dilution, partial excess energies and gas-liquid partition coefficient.

Chapter 3 presents all the experimental process, material used, methods applied, and results, including the physicochemical properties mentioned earlier, selectivities, capacities, which are briefly discussed. Chapter 4 concludes the work and suggests possible next steps to further advances in the area.

Chapter 2. State of the art

2.1. Terpenes and their separation processes

Terpenes and terpenoids are organic compounds found in various plant matrices, especially as constituents of essential oils. Terpenes can be categorized as unsaturated acyclic, monocyclic, or polycyclic hydrocarbons, while terpenoids are oxygenated derivatives, including functional groups such as aldehydes, alcohols, carboxylic acids, ethers and ketones [1]. Although their presence is relevant, terpenes can also provide some problems due to its low solubility in aqueous and alcoholic solution and to their oxidation processes, which results in a deterioration aroma and flavor [10]. On the other hand, terpenoids, being more polar, may be more desirable in certain products. For example, the essential oils from citrus peel are composed of about 90% of monoterpenes, however the organoleptic aspects are due to the few terpenoids and other oxygenated substances [10,13].

Being present in human history since the Egyptians [14], those compounds are still relevant to our society as ingredients in the pharmaceutical, perfumery, food and other industries [1,11]. For example, trolamine, menthol and camphor are terpene and terpenoids commonly used in non-prescript medication like Sportscreme Pain Relieving Rub (contains trolamine) and Salonpas Pain Patch (contains menthol and camphor), the last being a famous analgesic [15]. Other studies [16] show antimicrobial activities of terpenes obtained from the bark of *Ceasalpinia pulcherrina*, providing a potential new method to eliminate harmful bacteria and fungi other than the conventional antibiotics. Rubber, a polyterpene, is used mainly for its elastic properties. Additionally, since Charles Goodyear led the addiction of sulfur to rubber in a various degrees of mixture, the vulcanized rubber was developed, widening its application [14]. Another example is Patchoulol, an alcohol terpenoid found in the essential oil Patchouli, which is used to synthesize Taxol, a chemotherapy drug [1].

Both terpenes and terpenoids can be classified according to the number of isoprene (C_5H_8) units present. Therefore, a hemiterpene is a molecule with one isoprene unit, like isoprene itself and isoprenol, a monoterpene has two isoprene units, summing 10 carbon atoms like α -pinene and menthol, a sesquiterpene presents three isoprene units, a diterpene, four, and so on. Rubber, as mentioned previously, is a polyterpene, which means it is composed of, at least, 100 isoprene units

summing up to 500 carbon atoms [14,17]. Figure 1 shows how the isoprene units and the original backbone can be traced out in five examples.

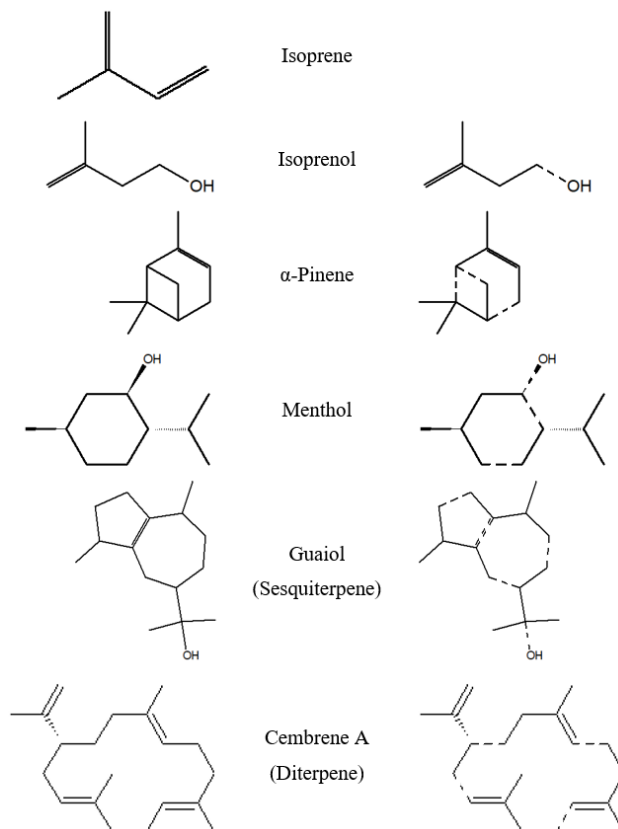


Figure 1 – Examples of the categorization of terpenes in terms of chemical structures.

As mentioned before, terpenes and terpenoids are used in combination for the most diverse applications; however, pure compounds are needed for many applications. The processes used to separate monoterpenes and other less polar substances from essential oils are called deterpenation. These processes result in more stable products, one rich in terpenes and another rich in oxygenated compounds [1,8]. In 2017, Martins [1] listed some of the separation methods applied to remove hydrocarbons from essential oils, which are vacuum distillation, membrane-based processes, supercritical extraction and liquid-liquid extraction.

In 2013, Martins et al. [18] used the vacuum distillation process to deterpenize orange essential oils, aiming to separate limonene, linalool and decanal. The distillation method is based on the different volatilities of the compounds. However, there are mixtures whose compounds have very low differences between their vapor pressure values, requiring a series of multiple distillation steps. The vacuum is usually applied to these kinds of mixtures, which may not reduce the number

of required distillation procedures, but it lowers the required temperature while promoting the thermal stability of the compounds.

In 2005, Diaz et al [19] studied the deterpenation of orange peel with supercritical fluid extraction using carbon dioxide as the solvent. The main compounds present in the orange peel are limonene, α -pinene, linalool, which are terpenes and terpenoids, and decanal. The method, being a fluid extraction, is theoretically close to the liquid-liquid extraction mentioned earlier; however, by using a supercritical fluid, its extraction capacity is often amplified. The less polar solutes present in the matrix are carried by the extraction fluid (in this case, carbon dioxide), but as a supercritical fluid can diffuse in solids like a gas and dissolve compounds like liquids, the matrix can be solid. Liquid-liquid extraction to fractionate lemon essential oil, which is mostly composed of limonene, γ -terpinene, β -pinene, citral and β -bisabolene, was studied by Koshima et al. [20] during 2012. The method uses two immiscible liquids, the oil matrix and an extraction solvent. The oil matrix carries the solutes that are partitioned depending on the polar affinity between the solutes and each of the liquids [7].

Between all possible mixtures of terpenes, there are some interesting mixtures to mention: α -pinene/ β -pinene and limonene/linalool. Both mixtures have compounds presenting very similar physical-chemical properties which make them difficult to separate, being also very interesting model mixtures. They are found, respectively, in pine essential oils [11] and citrus essential oils [21].

The first mixture is mostly found in turpentine, an essential oil originated from pine trees and an important sub-product of the paper pulp industry. Turpentine by itself is used as organic solvent for paints, perfumery and pharmaceutical ingredients [1,22]. On the other hand, α -pinene and β -pinene, individually, are normally used for synthesis of other compounds of commercial interest, for example, β -pinene act as feedstock for production of menthol and α -pinene, for camphor [17]. Other studies also show the uses of these two compounds for acrylic copolymers [23] or more complex molecules [24]. The separation of the α -pinene/ β -pinene mixture was studied by Díaz et al. [11]. The work aims to assess the interactions of the multiple compounds present in the pine essential oil (including α -pinene and β -pinene) by gas-liquid chromatography (GLC) with six different liquid phases (dinonyl phthalate, amine 220, tricresyl phosphate (tcp), carbowax 6000, ethylene glycol phthalate, carbowax 1500) at three temperatures: 355.15 K, 375.15 K and 395.15 K.

The second mixture is particularly important for the food, perfumery and chemical industry in general. Limonene, in high purity, can work as flavoring agent and, in low purity, can be used as an organic solvent, and linalool is important for its citric odor. Limonene epoxide, a molecule derivate from limonene is relevant for organic synthesis [13].

The separation of the citrus mixture has already been studied by Sevgili et al. [21]. The work presents liquid-liquid equilibria (LLE), at 298.15 K, of ternary systems composed of limonene, linalool and one of four glycols (ethylene glycol, diethylene glycol, triethylene glycol or 1,2-propylene glycol), proposing them as separation agents for the citrus mixture. Arce et al. [25] studied LLE of multiple ternary systems involving limonene, linalool, water and ethanol at 298.15 K or using 2-aminoethanol at 298.15 K, 308.15 K and 318.15 K.

2.2. Separation agents

2.2.1. Ionic liquids

Very intensively studied during the last two decades, ionic liquids (ILs), also known as room temperature ionic liquids (RTILs) or liquid salts, are normally composed of large and unsymmetrical organic cations, and an organic or inorganic anions, having their melting point below 100 °C [9]. The 1-tetradecyl-3-methylimidazolium tetrafluoroborate ($[C_{14}MIM][BF_4]$) is an example of IL, presented in the Figure 2.

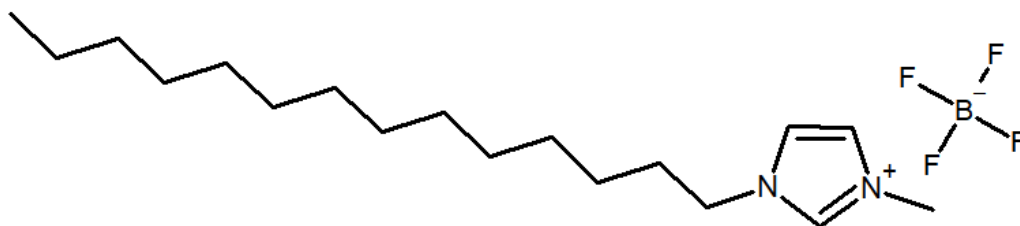


Figure 2 – Structure of 1-tetradecyl-3-methylimidazolium tetrafluoroborate .

Like mentioned above, ions can be either organic or inorganic, yielding an extremely large number of possible combinations, being possible to design properties as polarity, miscibility or solubility. Additionally, in general, ILs have negligible vapour pressure, high thermal stability at high temperature (if compared with organic solvents) and are mostly non-flammable [9,26]. However, not all ILs represent the greenest option as separation agents, as some are toxic and present very

poor biodegradability [7,27]. Nevertheless, ILs deservedly earn the title of “designer solvent” for such a fine-tuning of their properties and applications [7,26].

Marsh and Lichtenthaler [5] presented a review about RTILs, showing how its properties may vary through such a vast number of possible combinations, with many applications concerning liquid-liquid equilibria with organic solvents and gas solubility. After during 2010, Marciniak [6] made an extensive review detailing the influence of both the cation and anion of the IL on the activity coefficient of many different compounds (alkanes, alkene and aromatic organic molecules) and the selectivity of some mixtures of those compounds. In 2012, Pereiro et al. [7] presented a detailed review discussing the benefits of using ILs regarding its nature, properties and process efficiency on the separation of different azeotropic mixtures.

To assist the preliminary selection of solvents and, then, the design of new separation processes, it is desirable to have a priori information about the selectivity or capacity of a given solvent. Part of that thermodynamic information can be obtained by gas-liquid chromatography (GLC). For example, in 2016, Martins et al. [12] used GLC to obtain the activity coefficient of multiple terpenes and terpenoids, including α -pinene, β -pinene, eucalyptol, menthone and linalool in different ionic liquids as stationary phase ([C₄mim]Cl, [C₄mim][CH₃SO₃], [C₄mim][(CH₃)₂PO₄] and [C₄mim][CF₃SO₃]). Chromatography needs two phases, a mobile inert phase and a stationary phase. The retention time of a given solute is related to the intermolecular interactions between the solute and the stationary phase (with more or less affinity), since the mobile inert phase is expected not to interact with the solute. The unique behavior of each compound can be quantified as a separation coefficient, classifying the stationary phase as a good or bad entrainer.

The selection of such entrainers can be quite overwhelming, as the number of possibilities is huge. However, the Conductor-like Screening Model for Real Solvents (COSMO-RS) method is of great help concerning this analysis. It predicts thermophysical properties of fluid and liquid mixtures, being also able to predict activity or partition coefficients and phase diagrams of fluid systems [28]. Martins [1] used COSMO-RS to predict the ability of ILs (cations and anions) to be used as separation agents for terpenes and terpenoids. From the cations and anions studied, the cation trihexyltetradecylphosphonium, [P_{6,6,6,14}]⁺ and the anions bis(2,4,4-trimethylpentyl)phosphinate, [(C₈H₁₇)₂PO₂]⁻, or acetate, [OAc]⁻, were indicated to be the most promising. The present work will focus in testing the above-mentioned cation combined with the

anion $[(C_8H_{17})_2PO_2]^-$ or chloride, $[Cl]^-$, commercially named, respectively, as Cyphos[®] IL 104 and Cyphos[®] IL 101.

A search over studies on infinite dilution activity coefficients of different solutes in ILs constituted by at least one of these ions showed a few results only. Letcher et al. [4] obtained activity coefficients at infinite dilution of 14 solutes (n-alkanes, alk-1-enes, alk-1-yne, cycloalkanes and aromatic hydrocarbons) in the Cyphos[®] IL 104, using gas-chromatography at four temperatures ranging from 303.15 K to 318.15 K. The authors also determined the partial molar excess enthalpies at infinite dilution and selectivities comparing the different solutes. Banerjee and Khanna [3] determined activity coefficients at infinite dilution of 16 solutes (n-alkanes, alk-1-enes, cycloalkanes, alcohols and aromatic hydrocarbons), in three ILs, including Cyphos[®] IL 101, using gas-chromatography at three different temperatures: 308.15 K, 318.15 K and 328.15 K. The authors also calculated the partial molar excess properties at infinite dilution and compared the activities coefficients obtained with those predicted by COSMO-RS. Even though the predictions made in COSMO-RS confirmed the experimental results, proving the nonpolar behavior of phosphonium-based ILs, those ILs showed poor performance for separation processes regarding aliphatic and aromatic mixtures. The only exception was the trihexyl(tetradecyl)phosphonium-tetrafluoroborate $[P_{6,6,6,14}][BF_4]$, which presented moderate selectivity for benzene-alcohol mixtures.

Regarding other physicochemical properties, Neves et al. [29] determined the density, viscosity and solubility in water of seven different trihexyl(tetradecyl)phosphonium-based ($[P_{6,6,6,14}]^+$) ILs, including both Cyphos[®] IL 104 and 101, at 298.15 K.

2.2.2. Eutectic solvents

Other examples of separation agents are (deep) eutectic solvents (DES), which can have similar properties to ILs; however, they are multicomponent mixtures, not single compounds like ILs. Examples of common types of DESs are mixtures containing at least one ammonium salt, often choline chloride ($[Ch]Cl$) as shown in Figure 3 [1], like in the well-studied choline chloride/urea eutectic system [30].

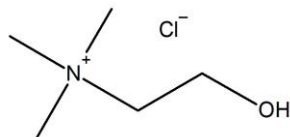


Figure 3 - Structure of choline chloride.

Depending on the compounds, these mixtures may have a much lower melting point than any of their pure components. At a certain molar ratio, the mixture reaches the lowest possible melting temperature, called eutectic point. DES, like ILs, have a high number of possible combinations, being able to be tailored to obtain certain physicochemical properties like viscosity, density, surface tension and polarity. Depending on the initial components, DESs may have a lower cost as no synthesis step is needed, being characterized as a “green solvent” [31,32]. In 2003, Abbott et al. [30] presented a seminal study about the choline chloride/urea mixture. The components, [Ch]Cl and urea, have melting points of 302 °C [30] and 133 °C [30], respectively, but, at a 1:2 molar ratio, the mixture melts at 12 °C. The authors also showed the dissolution versatility of this mixture, observing high solubilities of inorganic salts (LiCl), aromatic acids (benzoic acid), amino acids (d-alanine) and salts with poor solubility in water (AgCl).

In a separation process, ILs and DES can work as agents to enhance its efficiency. Pena-Pereira [2] presented a review showing multiple examples of separation processes that applied ILs and DES as separation agents. Additionally, in 2015, Tang et al. [33] focused their review in separation processes of biodiesel, aromatic hydrocarbons, gases, bioactive compounds and metals assisted by DES.

The use of ILs as separation agents for terpenes have already been investigated and several reviews and articles address the topic [1,8–12]. However, the use of DESs for the same purpose is a newer topic [34,35].

2.3. Determination of physicochemical properties

From the different methods usually used to obtain activity coefficients, the present work will focus on the gas-liquid chromatography (GLC) method. Using a gas chromatograph (GC), activity coefficients at infinite dilution (γ_{13}^{∞} or IDAC) in a given stationary phase can be calculated from the retention volume of each solute [12,36], through Equation (1), developed by Everett [37] and Cruickshank et al. [38]:

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

where n_3 is the number of moles of solvent on the column packing, R is the ideal gas constant, T is the GC oven 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 at 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 crossed second virial coefficient of the solute and the carrier gas, and V_1^{∞} is the partial molar volume of the solute at infinite dilution in the solvent.

The pressure correction J_2^3 is calculated through Equation 2 also presented by Everett [37].

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

In this last equation P_i is the inlet pressure. The net retention volume V_N is calculated through Equation 3.

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

In which t_s and t_g are, respectively, the retention times of the solute and the unretained gas, and U_0 is the column outlet volumetric flow rate, which can be calculated with Equation 4.

$$U_0 = U \frac{P_M T}{P_o T_M} \quad (4)$$

In which U , P_M and T_M are, respectively, the volumetric flow rate, pressure and temperature measured by the flowmeter, in our case at the outlet stream after the detector. In order to estimate the column outlet pressure (P_o), a linear correlation between the pressure drop value (ΔP) and the volumetric flow rate was established at different temperatures as defined in Equation 5. The coefficients (A and B) are presented in Table A.1 of Appendix A.

$$\Delta P = P_o - P_M = AU + B \quad (5)$$

Additionally, once the activity coefficients at infinite dilution are determined, the partial excess properties (Gibbs free energy $\bar{G}_m^{E,\infty}$, enthalpy $\bar{H}_m^{E,\infty}$ and entropy $\bar{S}_m^{E,\infty}$), selectivities S_{ij}^{∞} and capacities k_j^{∞} can be calculated through Equations 6 to 10 [1,12].

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

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

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

$$S_{ij}^\infty = \frac{\gamma_i^\infty}{\gamma_j^\infty} \quad (9)$$

$$k_j^\infty = \frac{1}{\gamma_j^\infty} \quad (10)$$

In which j is the solute with smaller activity coefficient at infinite dilution in the IL when comparing compounds i and j .

Another property that can be calculated is the gas-liquid partition coefficient $K_L = (c_1^L/c_1^G)$ for each solute between the carrier gas and the ionic liquid. It can be calculated through Equation 11.

$$\ln(K_L) = \ln\left(\frac{V_N \rho_3}{m_3}\right) - \frac{P_o J_2^3 (2B_{12} - V_1^\infty)}{RT} \quad (11)$$

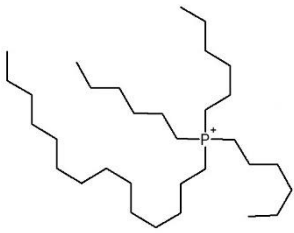
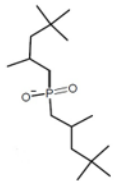
In which ρ_3 is the density of the ionic liquid.

Chapter 3. Experimental work

3.1. Materials

The extensive list of 45 solutes (source and mass fraction purity) is presented in Appendix B (Table B.1). The ILs used were, as mentioned earlier, [P_{6,6,6,14}] [(C₈H₁₇)₂PO₂] (CAS Number 465527-59-7) and [P_{6,6,6,14}] Cl (CAS Number 258864-54-9). Their structure, source and purities are shown in Table 3.1.

Table 3.1 - Structure, source and purities of the ILs used.

Chemical Formula		Chemical Name	Supplier	M (g.mol ⁻¹)	Purity ^a (mass %)
Cation	Anion				
		trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate	Cytec	773.27	≥ 0.93
	Cl ⁻	trihexyl(tetradecyl)phosphonium chloride	Cytec	519.31	≥ 0.91

^aDeclared by the supplier.

3.2. Experimental method

The infinite dilution activity coefficients were determined from the retention times of the solute and unretained gas (t_s and t_g , respectively) measured using a Varian CP-3380 gas chromatograph, equipped with a heated on-column 1041 injector and a thermal conductivity detector (TCD), and applying the GLC method detailed previously [39]. The inlet pressure (P_i) on the column was measured by a Swagelok S Model Transducer with an accuracy of 0.5% of span limit point calibration. Helium was used as carrier gas and an Agilent Technologies precision gas flow meter (Part Number 5973-1712) was placed after the TCD in order to measure the volumetric flow (U), temperature (T_M) and pressure (P_M) from that outlet stream. The accuracy of the equipment is ± 1.0 cm³.min⁻¹ for the volumetric flow rate, ± 0.01 K for the temperature and ± 0.01 psia for the pressure. The injector and TCD temperatures were adjusted according to the boiling point temperature of the solutes, being kept, respectively, between 473.15 K and 523.15 K for alkanes, cycloalkanes, ketones, ethers, cycloethers, aromatic hydrocarbons, esters, acetonitrile, pyridine and thiophene, between 553.15 K and 573.15 K for water, alcohols and terpenes/terpenoids with lower boiling

point, and between 553.15 K and 593.15 K for the terpenoids with higher boiling point. The volumetric flow rate was also adjusted according to the retention time difference between the solute and unretained gas ($t_s - t_g$). The flow rate used was approximately $100 \text{ cm}^3 \text{ min}^{-1}$, being lowered up to $30 \text{ cm}^3 \text{ min}^{-1}$ if the time difference was smaller than 1 min. Additionally, some of the terpenoids high boiling point are solid at room temperature, therefore they were diluted in alcoholic solvents to inject them in the GC, borneol and menthol were diluted in ethanol while camphor was diluted in 2-propanol.

The chromatographic columns were prepared in collaboration with laboratory CICECO at the University of Aveiro. The stationary phase was packed in a glass column to contain between 45% to 50% of IL (in mass) coated onto a 100-120 mesh Chromosorb W/AW – DMCS solid support material. This preparation method can be found in more detail elsewhere [1,40]. All glass columns had 1 m of length and 4 mm of internal diameter. In Figure 4 is shown one Cyphos® IL 104 column used, already installed inside the gas chromatograph. In order to ensure the infinite dilution conditions, each injection contained approximately $0.2 \mu\text{L}$ of the solute and $0.8 \mu\text{L}$ of air, which was used as the unretained gas, except for the diluted solutes, whose injection contained $0.8 \mu\text{L}$ of the solute and $0.2 \mu\text{L}$ of air.

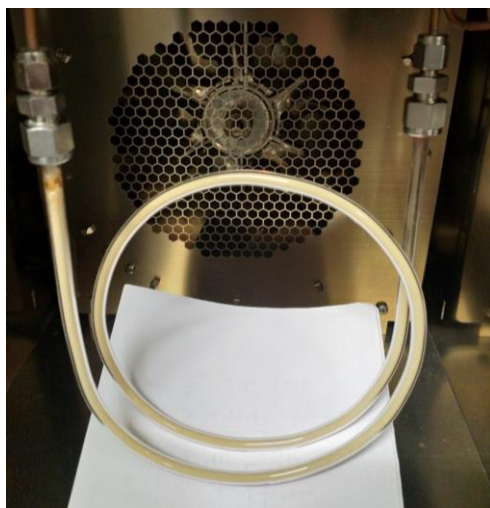


Figure 4 - Chromatographic column installed in the GC.

Four chromatographic columns were prepared, two for each IL. The first column of each IL was used for testing, being injected only 11 of the 45 solutes, to obtain γ_{13}^{∞} data at 3 different temperatures: n-octane, cyclohexane, toluene, THF, acetone, ethyl acetate and acetonitrile at

343.15 K, 363.15 K and 383.15 K and methanol, 2-propanol, water and α -pinene at 383.15 K, 393.15 K and 403.15 K. The second column was fully tested, being injected all 45 solutes, being obtained γ_{13}^{∞} data at least for five different oven temperatures (with some exceptions). Due to Cyphos® IL 104 thermal instability at higher temperatures, some terpenes with higher boiling temperatures could not be injected, so the chosen temperatures to obtain γ_{13}^{∞} data were from 333.15 K to 383.15 K for alkanes, cycloalkanes, ketones, ethers, cycloethers, aromatic hydrocarbons, esters, acetonitrile, pyridine and thiophene and from 363.15 K to 413.15 K for water, alcohols, terpenes and terpenoids. Since the Cyphos® IL 101 presented a higher thermal stability, all terpenes could be injected, so the chosen temperatures to obtain γ_{13}^{∞} data were from 333.15 K to 383.15 K for alkanes, cycloalkanes, ketones, ethers, cycloethers, aromatic hydrocarbons, esters, acetonitrile, pyridine and thiophene, from 363.15 K to 413.15 K for water and alcohols, and from 383.15 K to 458.15 K for terpenes and terpenoids.

3.3. Experimental results

3.3.1. Activity coefficients at infinite dilution

All γ_{13}^{∞} data measured is shown in Appendix C (Table C.1 and Table C.2). Unfortunately, due to the relatively high boiling temperature of some terpenes and terpenoids, and the thermal instability of the IL at high temperatures, it was not possible to determinate values γ_{13}^{∞} at five different temperatures, for most of the terpenes and terpenoids.

Very good linear correlation between $\ln(\gamma_{13}^{\infty})$ and $1/T$ was observed (with some exceptions), which is a common feature among most solutes, and like shown in the literature for many of the solvents also. It is also noticeable the different behavior for different categories of solutes: non-polar (NP), polar and non-associative (NA) and polar and self-associative (AS). For a molecule to be self-associative, it must have both hydrogen bond acceptors and donors, while polar non-associative only present either hydrogen bond acceptor or donors.

Solutes with NP characteristics, like n-alkanes and aromatic hydrocarbons, show a small or zero slope. Solutes with NA characteristics, like acetonitrile, ketones and esters, show positive slopes. Lastly, solutes with AS characteristics, like alcohols and water, show a strongly negative slope. Figure 5 shows the $\ln(\gamma_{13}^{\infty})$ at different temperatures of six solutes from different families in Cyphos® IL 104 and Cyphos® IL 101: n-nonane (n-alkane), toluene (aromatic hydrocarbon), diethyl ether (ether), acetone (ketone), ethyl acetate (ester) and α -pinene (terpene). It is important

to note that the slope in the linear relation of the different solutes keeps mostly similar in both ILs, however the values of $\ln(\gamma_{13}^{\infty})$ can vary significantly.

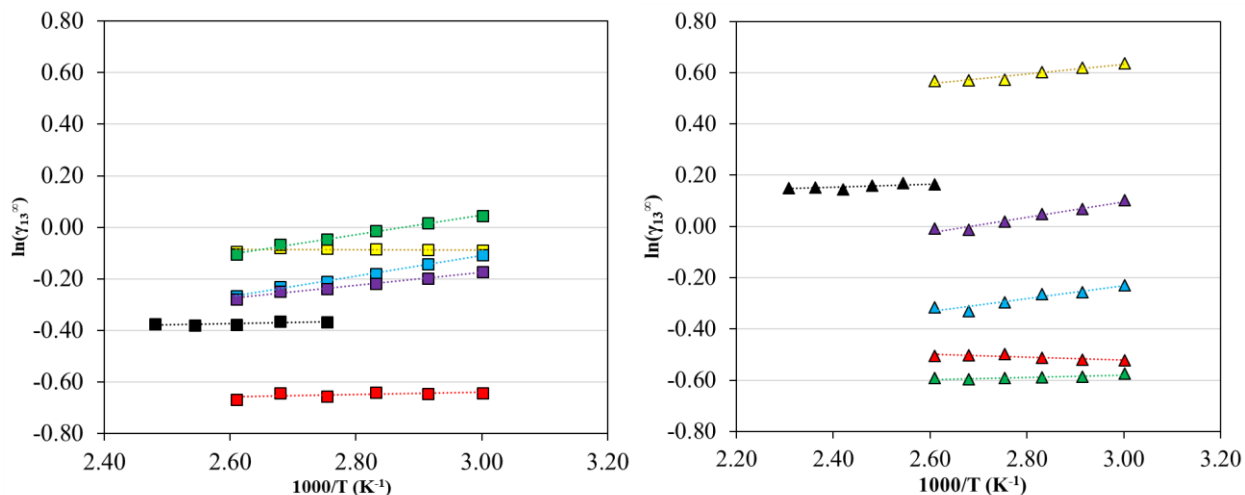


Figure 5 - $\ln(\gamma_{13}^{\infty})$ of various solutes in Cyphos® IL 104 in the left panel and in Cyphos® IL101 in the right panel both as a function of $1/T$. Color Code: ● Nonane; ● Toluene; ● Acetonitrile; ● Acetone; ● Ethyl Acetate; ● α -Pinene.

The value of $\ln(\gamma_{13}^{\infty})$ is related to the degree of deviation from ideality. A value of $\ln(\gamma_{13}^{\infty})$ equal to zero, means that the solution presents no deviations from ideality. Therefore, the interactions between the different compounds in the solution are as similar as the ones between the pure compounds. However, values of $\ln(\gamma_{13}^{\infty})$ higher than zero imply positive deviations from ideality, and naturally values lower than zero imply negative deviations. Therefore, lower values of $\ln(\gamma_{13}^{\infty})$ suggest that the solute has a stronger interaction with molecules of IL than with itself. According to this interpretation, most solutes presented in Figure 5 have stronger interactions with Cyphos® IL 104 than with IL 101.

It was also possible to notice patterns of behavior of solutes from the same functional group. Figure 6 shows the $\ln(\gamma_{13}^{\infty})$ of n-alkanes and aromatic hydrocarbons as function of temperature.

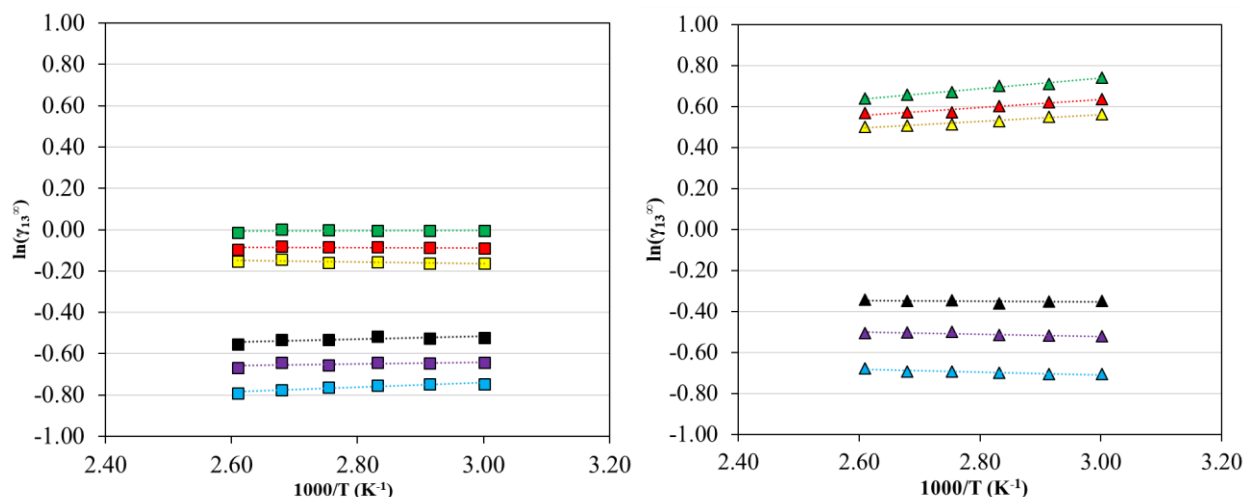


Figure 6 - $\ln(\gamma_{13}^{\infty})$ of n-alkanes and aromatic hydrocarbons in Cyphos® IL 104 in the left panel and in Cyphos® IL 101 in the right panel both as a function of $1/T$. Color Code: ● Octane; ● Nonane; ● Decane; ● Benzene; ● Toluene; ● Ethyl benzene.

Although both groups fall in the NP category, comparatively, the aromatic compounds are more polar than the n-alkanes, which are related to the π electrons. This polarity difference is experimentally observed in the slightly lower values of $\ln(\gamma_{13}^{\infty})$ that reflect a higher interaction in both ILs. This pattern is better shown in Figure 7, in which $\ln(\gamma_{13}^{\infty})$ of cycloalkanes and their aromatic counterpart are presented.

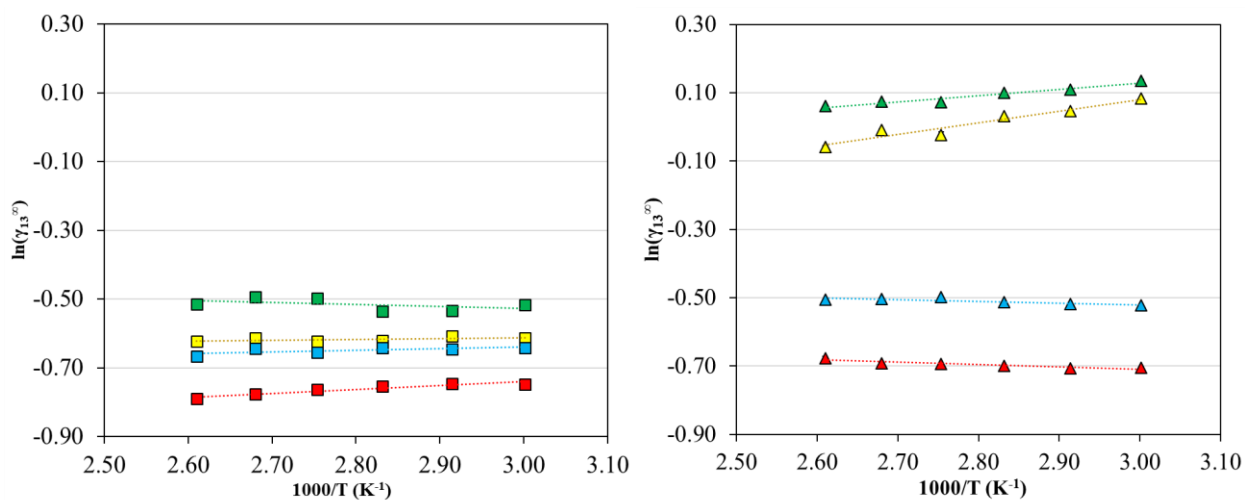


Figure 7 - $\ln(\gamma_{13}^{\infty})$ of cycloalkanes and aromatic hydrocarbons in Cyphos® IL 104 in the left panel and in Cyphos® IL 101 in the right panel both as a function of $1/T$. Color Code: ● Cyclohexane; ● Benzene; ● Methylcyclohexane; ● Toluene.

Clearly, both benzene and toluene infinite dilution activity coefficients are lower than cyclohexane and methylcyclohexane, respectively. Meanwhile, cyclohexane and methylcyclohexane show

greater interactions with Cyphos® IL 104 than with Cyphos® IL 101, like the alkanes. Another pattern can be observed in Figure 6, it shows a gradient behavior in both groups, presenting stronger interactions with both ILs for solutes with smaller carbon chains. In order to show another example of that behavior, Figure 8 shows $\ln(\gamma_{13}^{\infty})$ of various aromatic hydrocarbons with different number of atoms of carbon.

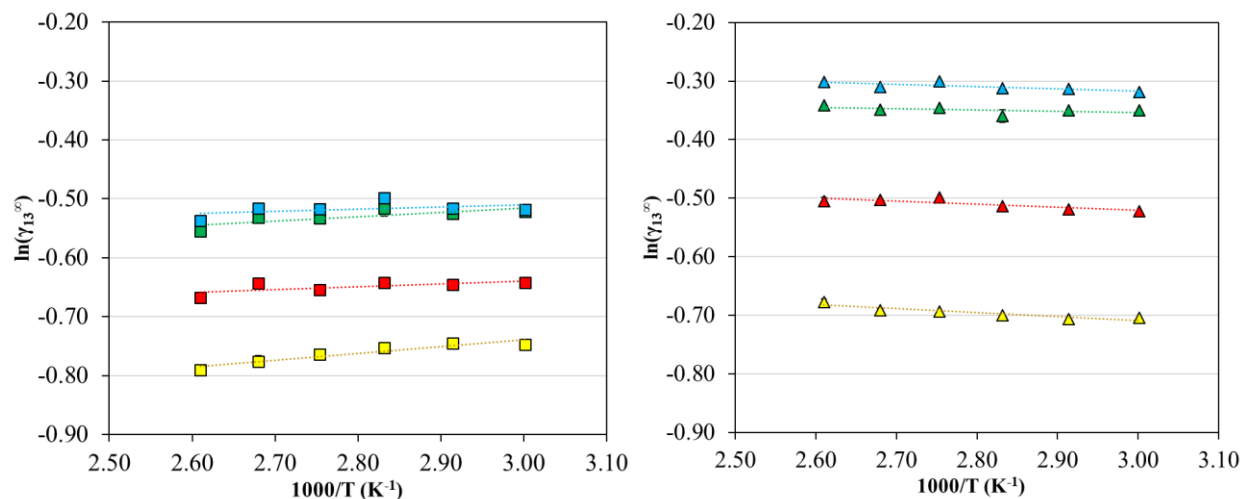


Figure 8 - $\ln(\gamma_{13}^{\infty})$ of aromatic hydrocarbons in Cyphos® IL 104 in the left panel and in Cyphos® IL 101 in the right panel both as a function of $1/T$. Color Code: ● Benzene; ● Toluene; ● Ethyl Benzene; ● p-Xylene.

It is noticeable that the number of carbon atoms outside the aromatic cycle causes more impact in the value of $\ln(\gamma_{13}^{\infty})$ than the position of side carbon atoms. However, in both ILs, the ethyl benzene data was lower than the data from p-xylene. Figure 9 presents $\ln(\gamma_{13}^{\infty})$ of ether solutes in both ILs.

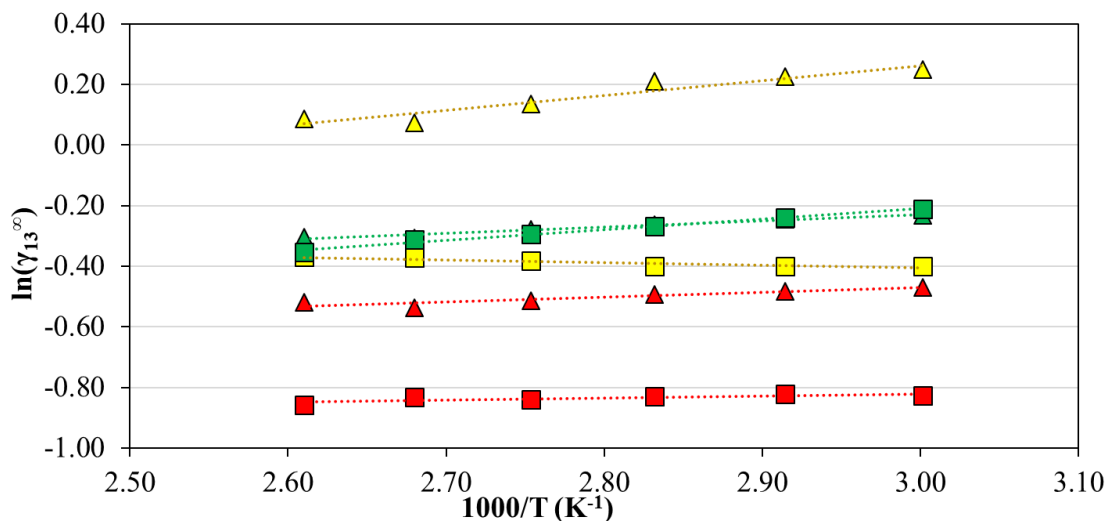


Figure 9 - $\ln(\gamma_{13}^{\infty})$ of different ethers as a function of $1/T$ in Cyphos® IL 104 (\square) and in Cyphos® IL 101 (Δ). Color Code: $\color{yellow}\blacktriangle$ Diethyl ether; $\color{red}\blacktriangle$ THF; $\color{green}\blacksquare$ 1,4-Dioxane.

Although diethyl ether, THF and 1,4-dioxane are all ethers, the first two show lower $\ln(\gamma_{13}^{\infty})$ data when in Cyphos® IL 104 than in Cyphos® IL 101, while the latter show almost no difference between the two different ILs. This behavior difference can be due to the first two solutes possess only one oxygen atom while the latter possess two. Furthermore, diethyl ether showed a slope difference between ILs while the other two ethers had almost no difference. This can be due to diethyl ether being acyclic while the other two are cyclic, therefore the temperature seems to have greater effects in Cyphos® IL 101 when applied on open chain ethers. Looking into other oxygenized compounds, Figure 10 shows $\ln(\gamma_{13}^{\infty})$ of various esters in both ILs.

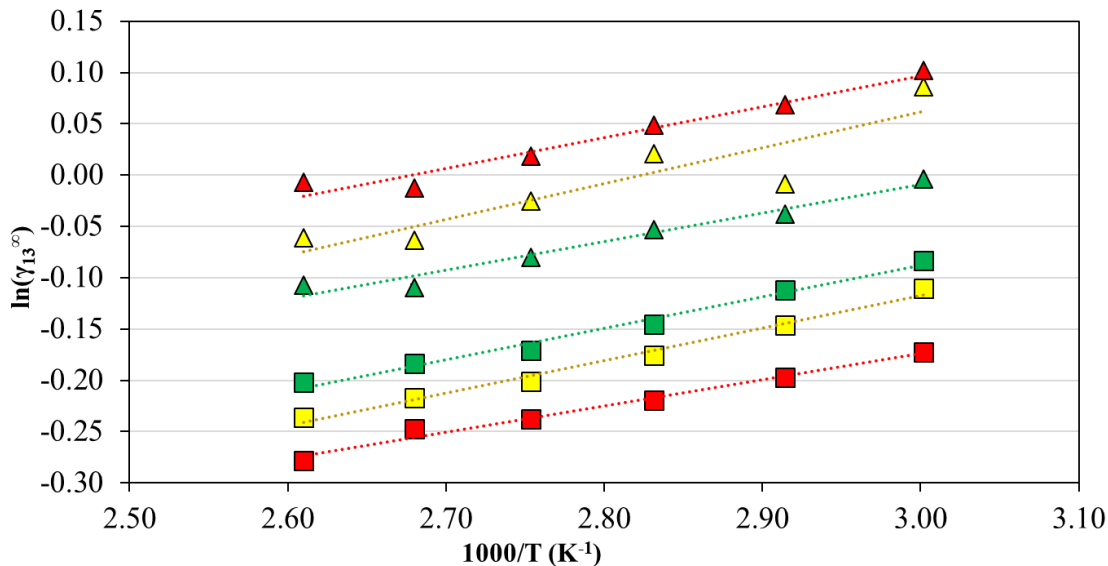


Figure 10 - $\ln(\gamma_{13}^{\infty})$ of different esters as a function of $1/T$ in Cyphos® IL 104 (\square) and in Cyphos® IL 101 (Δ). Color Code: $\color{yellow}\blacktriangle$ Methyl acetate; $\color{red}\blacktriangle$ Ethyl acetate; $\color{green}\blacktriangle$ Vinyl acetate.

The esters solutes show higher interactions in Cyphos® IL 104 than in Cyphos® IL 101 like most solutes tested, showing an almost symmetrical behavior. While the Cyphos® IL 104 has greater interactions with acetates with longer carbon chains, Cyphos® IL 101 has with acetates with smaller ones. In both ILs the vinyl acetate does not behave alongside the pattern described above, probably due to its unsaturated bond. Figure 11 and Figure 12 shows data of acetonitrile, pyridine and thiophene in order to observe the effects of nitrogen and sulfur atoms on $\ln(\gamma_{13}^{\infty})$ values in both ILs.

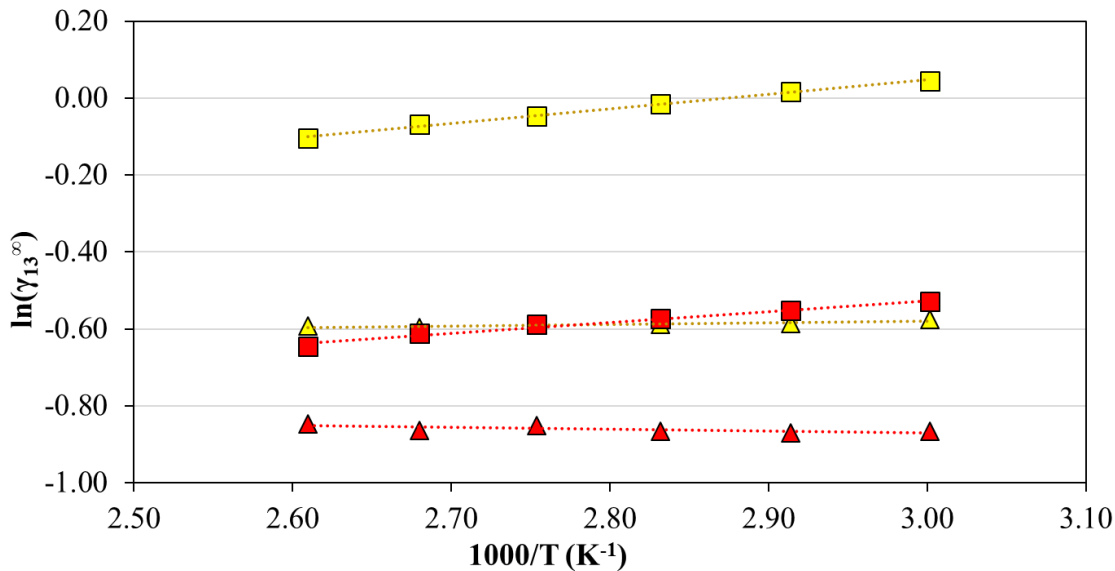


Figure 11 - $\ln(\gamma_{13}^{\infty})$ of acetonitrile and pyridine as a function of $1/T$ in Cyphos® IL 104 (□) and in Cyphos® IL 101 (Δ). Color Code: ● Acetonitrile; ● Pyridine.

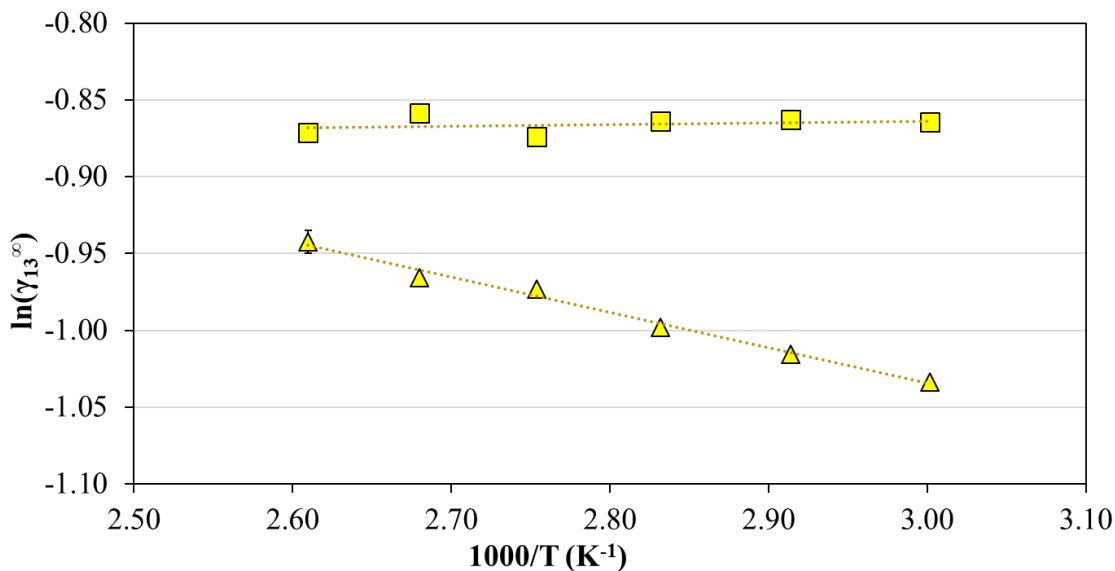


Figure 12 - $\ln(\gamma_{13}^{\infty})$ of thiophene as a function of $1/T$ in Cyphos® IL 104 (□) and in Cyphos® IL 101 (Δ).

It is worth noticing that the slope of the acetonitrile, pyridine and thiophene slightly changes between ILs. Unlike most of the other solutes, Cyphos® IL 101 showed a greater interaction with all three solutes when compared with Cyphos® IL 104. This behavior is also noticed with acetone data, shown in Figure 13 alongside butanone, the other ketone tested.

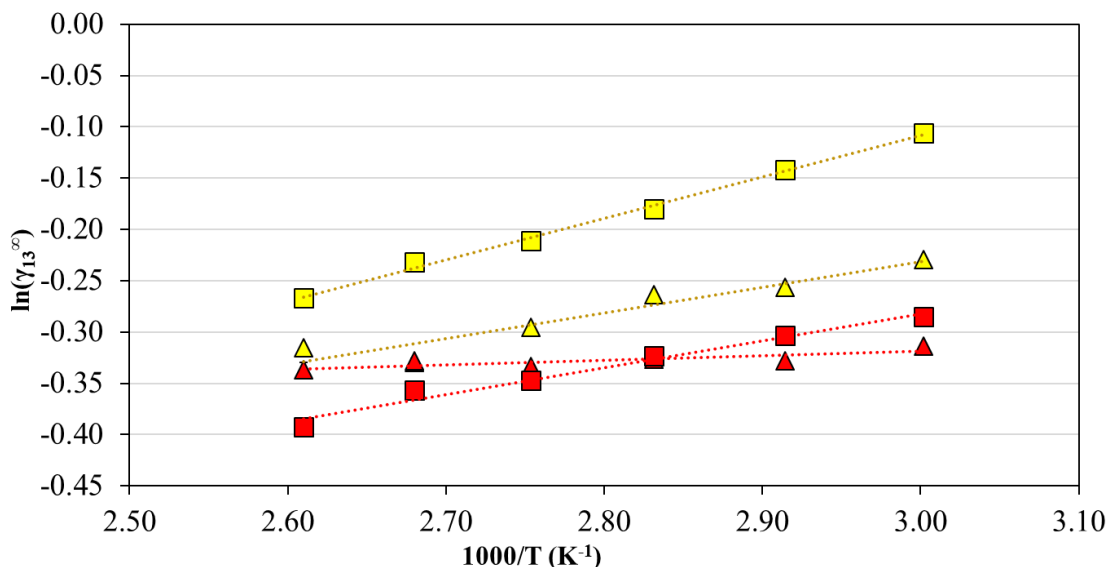


Figure 13 - $\ln(\gamma_{13}^{\infty})$ of ketone solutes as a function of $1/T$ in Cyphos® IL 104 (\square) and in Cyphos® IL 101 (Δ). Color Code: $\color{yellow}\bullet$ Propanone; $\color{red}\bullet$ Butanone.

The change of pattern for acetonitrile, pyridine, thiophene and ketone solutes can be due to the presence of a halogenic anion in Cyphos® IL 101, unlike Cyphos® IL 104 which has a wider organic anion. Additionally, Figure 13 also shows that butanone shifts the ILs with which has a stronger interaction around 80°C. This means that in temperatures higher than 80°C, Cyphos® IL 104 presents higher interactions with butanone, while in lower temperatures, Cyphos® IL 101 interactions are stronger.

Since a total of seven different alcoholic solutes were tested, more comparisons can be made in order to fathom the interactions between alcoholic solutes and ILs. Figure 14 presents the $\ln(\gamma_{13}^{\infty})$ of six alcohols, but it also shows three “sub-groups” of alcohols with closer values: methanol, the other primary alcohols and then secondary alcohols. The difference observed between the three “sub-groups”, more particularly between primary and secondary alcohols may be due to the steric hindrance of the hydroxyl group in the latter.

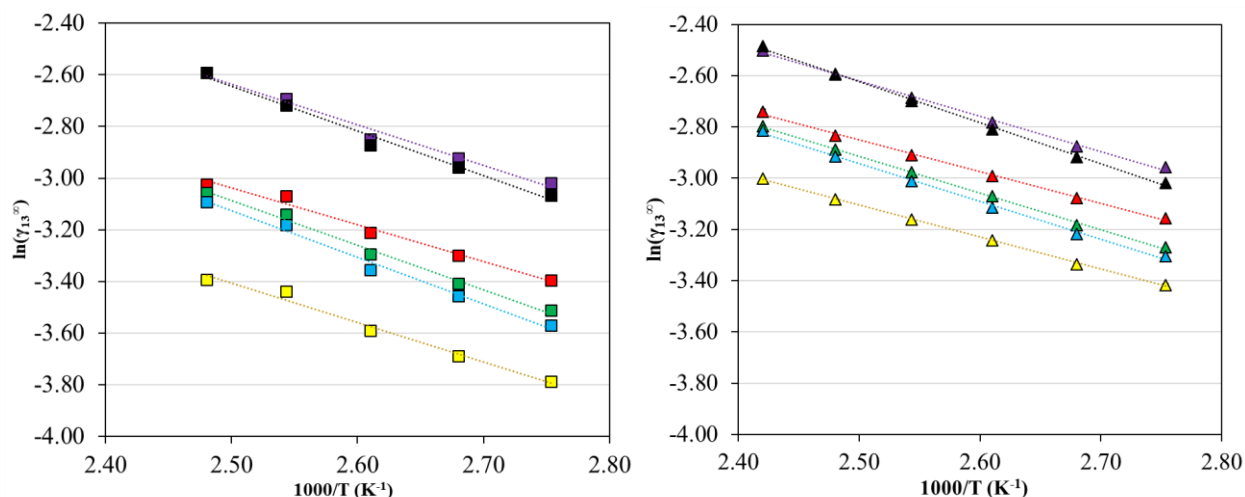


Figure 14 - $\ln(\gamma_{13}^{\infty})$ of selected alcohols as a function of $1/T$ in Cyphos® IL 104 in the left panel and in Cyphos® IL 101 in the right panel. Color Code: ● Methanol; ● Ethanol; ● 1-Propanol; ● 1-Butanol; ● 2-Propanol; ● 2-Butanol.

It is worth noticing that the alcoholic solutes showed significantly lower $\ln(\gamma_{13}^{\infty})$ values than any other solute, even some alcoholic terpenes behave likewise. However, it is not clear which is more relevant, the size of the carbon chain attached to the functional carbon or the nature of the alcohol (being primary, secondary etc.). To make this comparison clearer, Figure 15 shows $\ln(\gamma_{13}^{\infty})$ data of multiple alcoholic solutes with one limitation: the chain attached to the functional carbon have one carbon atom (methyl).

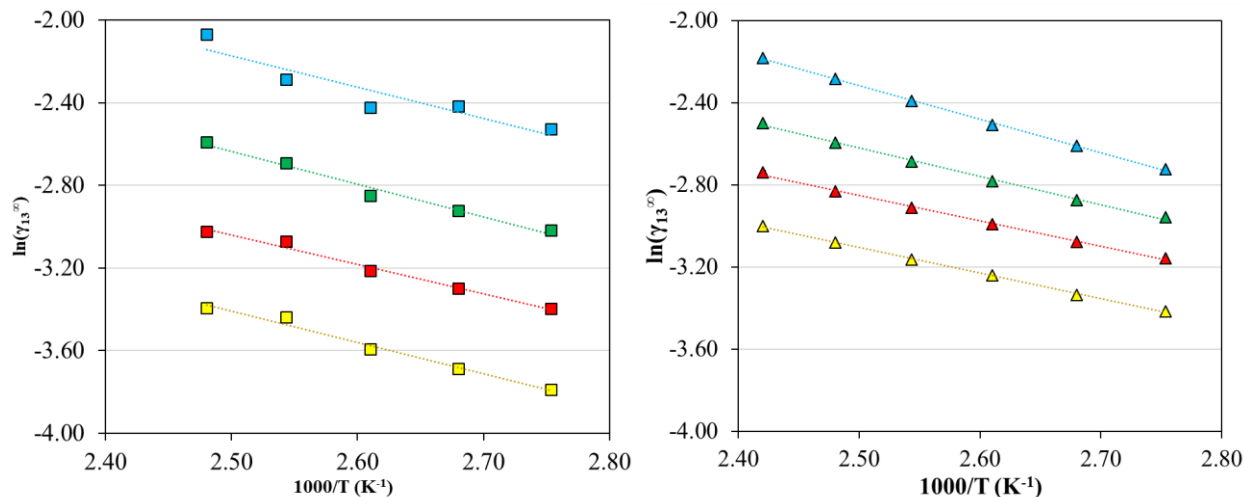


Figure 15 – $\ln(\gamma_{13}^{\infty})$ of different alcohols as a function of $1/T$ in Cyphos® IL 104 in the left panel and in Cyphos® IL 101 in the right panel. Color Code: ● Methanol; ● Ethanol; ● 2-Propanol; ● Tert-Butanol.

In both ILs the sequence maintains the same, in which methanol (the free carbon alcohol) has the greatest interaction, and tert-butanol (the tertiary alcohol) has the lowest interaction. In both cases

the spacing between the primary alcohols in Figure 14 is much lower than the ones presented in Figure 15. In order to look further for the comparison before mentioned, the total amount of carbons will be limited to four. Figure 16 shows data of multiple butanol with different structures.

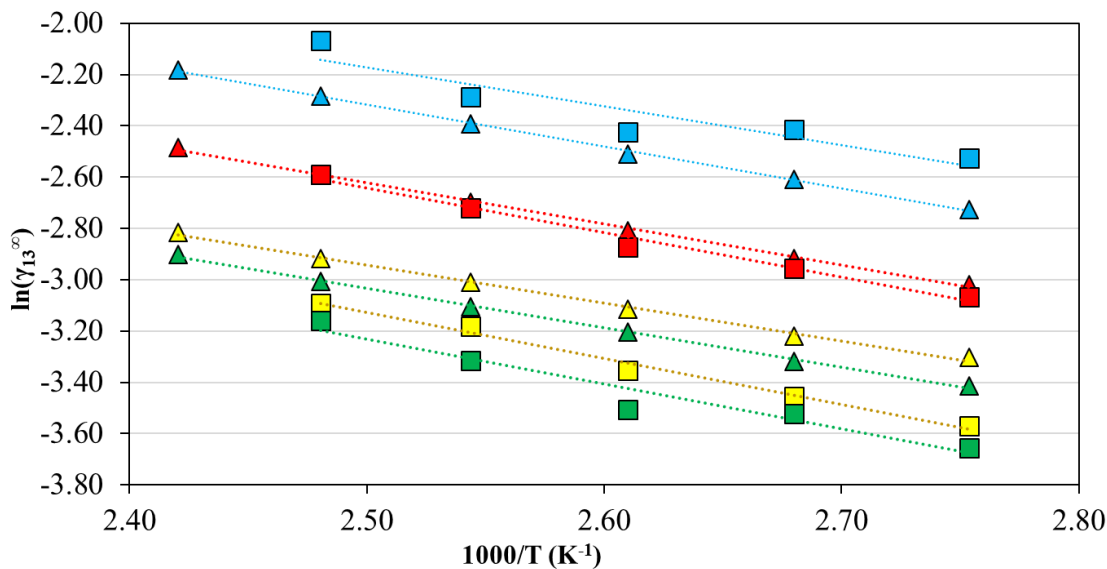


Figure 16 - $\ln(\gamma_{13}^{\infty})$ of butanols as a function of $1/T$ in Cyphos® IL 104 (\square) and in Cyphos® IL 101 (Δ). Color Code: \bullet 1-Butanol; \bullet 2-Butanol; \bullet Isobutanol; \bullet Tert-Butanol.

Both 1-butanol and isobutanol are primary alcohols and their data is much closer to each other than with the other compounds, a behavior that happens in both ILs. Therefore, analyzing both Figure 14 and Figure 15, it becomes clear that the nature of the alcohol is more relevant to the $\ln(\gamma_{13}^{\infty})$ value than the length and structure of the chains attached to the functional carbon, although the latter do has impact in said value. Additionally, Figure 16 shows how the nature of the alcohol affect the interactions with the ILs, the primary alcohols show greater interaction with Cyphos® IL 104, secondary alcohols have similar interactions in both ILs, and tertiary alcohols show greater interaction with Cyphos® IL 101.

Following with the terpenes and terpenoids, Figure 17 to Figure 20 show, respectively, $\ln(\gamma_{13}^{\infty})$ data of terpenes, etheric, ketone and alcohol based terpenoids. It was possible to obtain $\ln(\gamma_{13}^{\infty})$ data at six different temperatures for all terpenes in Cyphos® IL 101. Unfortunately, that was not the case for most terpenes in Cyphos® IL 104. As mentioned earlier, Cyphos® IL 104 showed poor thermal stability at high temperatures, which is necessary to obtain data for solutes with such high boiling point as terpenes.

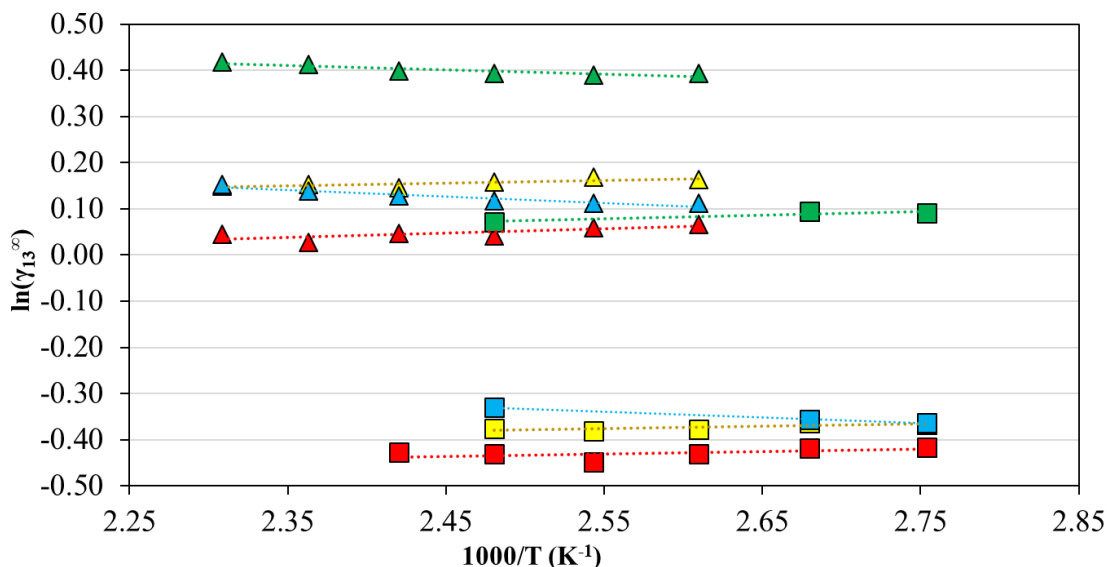


Figure 17 - $\ln(\gamma_{13}^{\infty})$ of terpenes as a function of $1/T$ in Cyphos® IL 104 (\square) and in Cyphos® IL 101 (Δ). Color Code: \bullet α -Pinene; \bullet β -Pinene; \bullet p-Cymene; \bullet (R)-(+)-Limonene.

Terpenes show almost no slope, similarly to the n-alkanes and cycloalkanes tested. Even though α -pinene and β -pinene have very similar molecular structure, which also explains such close $\ln(\gamma_{13}^{\infty})$ values, the latter shows greater interaction with both ILs. Additionally, all terpenes showed greater interactions with Cyphos® IL 104 than with Cyphos® IL 101.

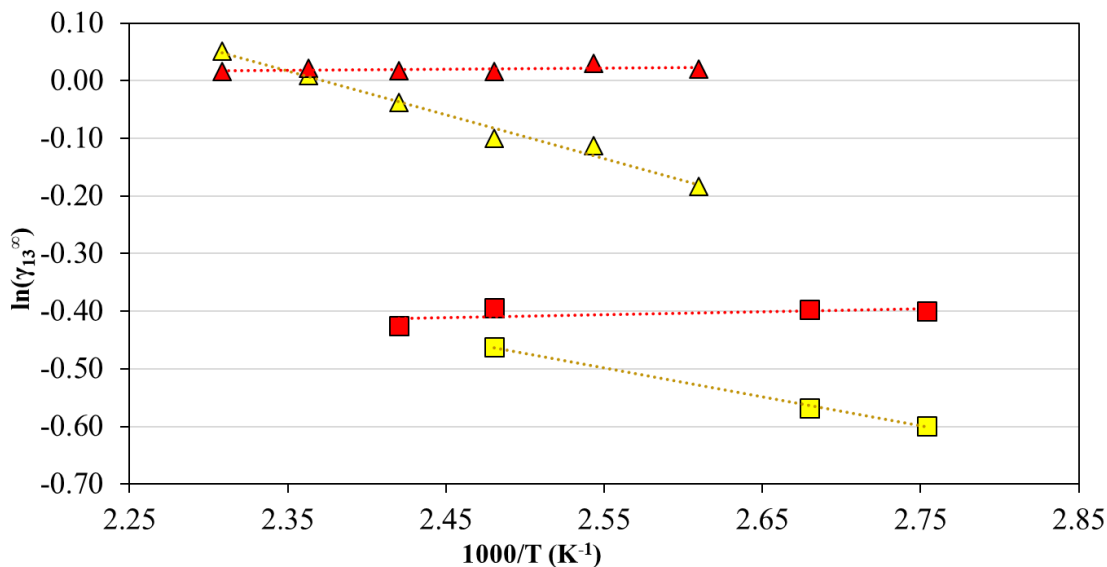


Figure 18 - $\ln(\gamma_{13}^{\infty})$ of ether terpenoids as a function of $1/T$ in Cyphos® IL 104 (\square) and in Cyphos® IL 101 (Δ). Color Code: \bullet α -Pinene Oxide; \bullet Eucalyptol.

As shown to most compounds, the ether terpenoids had greater interaction with Cyphos® IL 104 than with Cyphos® IL 101. Additionally, the slope of the compounds was similar in both ILs

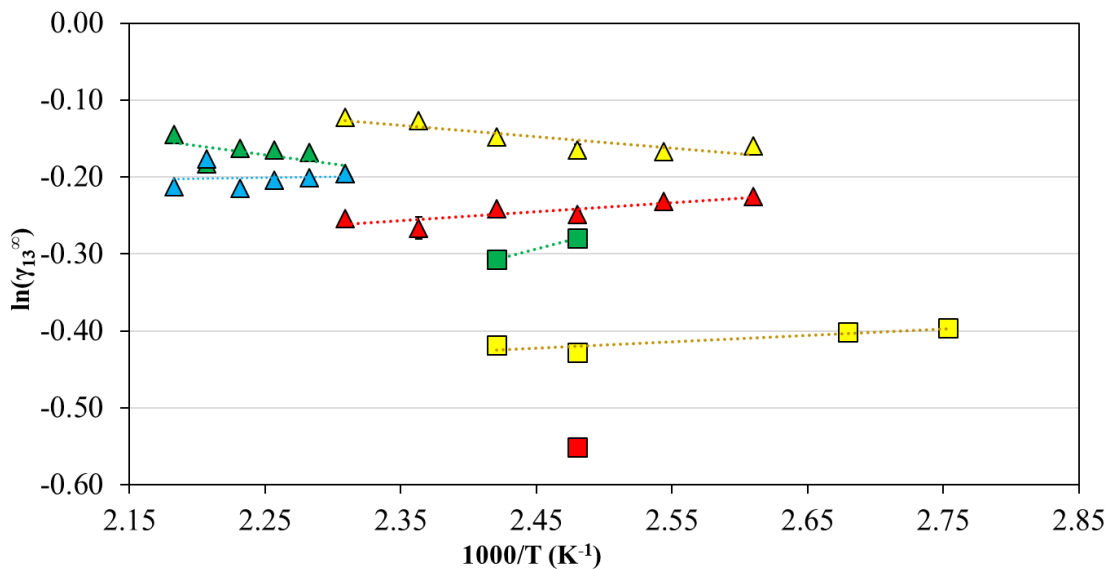


Figure 19 - $\ln(\gamma_{13}^{\infty})$ of ketone terpenoids as a function of $1/T$ in Cyphos® IL 104 (□) and in Cyphos® IL 101 (Δ). Color Code: ● (-)-Menthone; ● (R)-(-)-Fenchone; ● (S)-(+)-Carvone; ● (R)-(+)-Camphor.

It is important to note that the ketone terpenoids do not show the same behavior of other ketones compounds tested, since Cyphos® IL 104 showed greater interactions with all ketone terpenoids. That difference can be due to the other ketones have their functional carbon in an acyclic chain, while all terpenoids have theirs in a cyclic chain. Since just a few data could be gathered for fenchone and carvone, not much can be discussed about their slopes, however, menthone data showed a slight difference in slope between ILs.

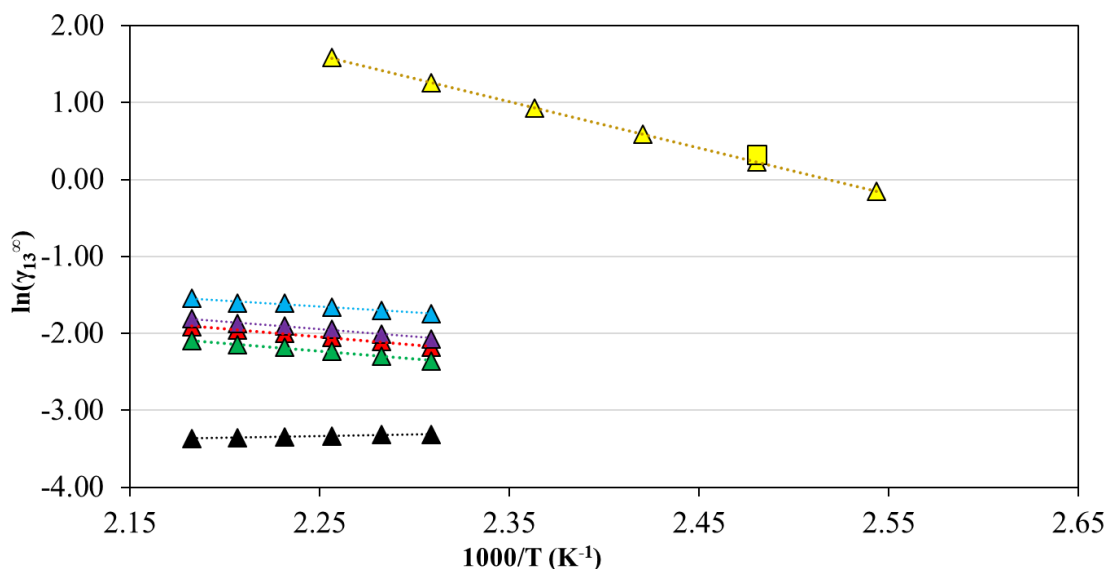


Figure 20 - $\ln(\gamma_{13}^{\infty})$ of alcoholic terpenoids as a function of $1/T$ in Cyphos® IL 104 (□) and in Cyphos® IL 101 (Δ). Color Code: ● Linalool; ● Geraniol; ● Citronellol; ● (-)-Isopulegol; ● (L)-(-)-Menthol; ● (-)-Borneol.

The first note in the Figure 20 is that while geraniol, citronellol, (-)-isopulegol and (L)-(-)-menthol have relatively close activity coefficients, linalool has its values much above and (-)-borneol, lower. Linalool is an acyclic tertiary alcohol, so the different behavior is expected as seen in the other alcoholic compounds tested, however such a steep slope was unexpected. Furthermore, since geraniol and citronellol are both primary alcohols, their data is expected to be close. However, since all alcohols tested before were acyclic, not much can be implied in order to analyze isopulegol, menthol and borneol data, since those three terpenoids are cyclic secondary alcohols. Finally, Figure 21 shows $\ln(\gamma_{13}^{\infty})$ data for water in both ILs.

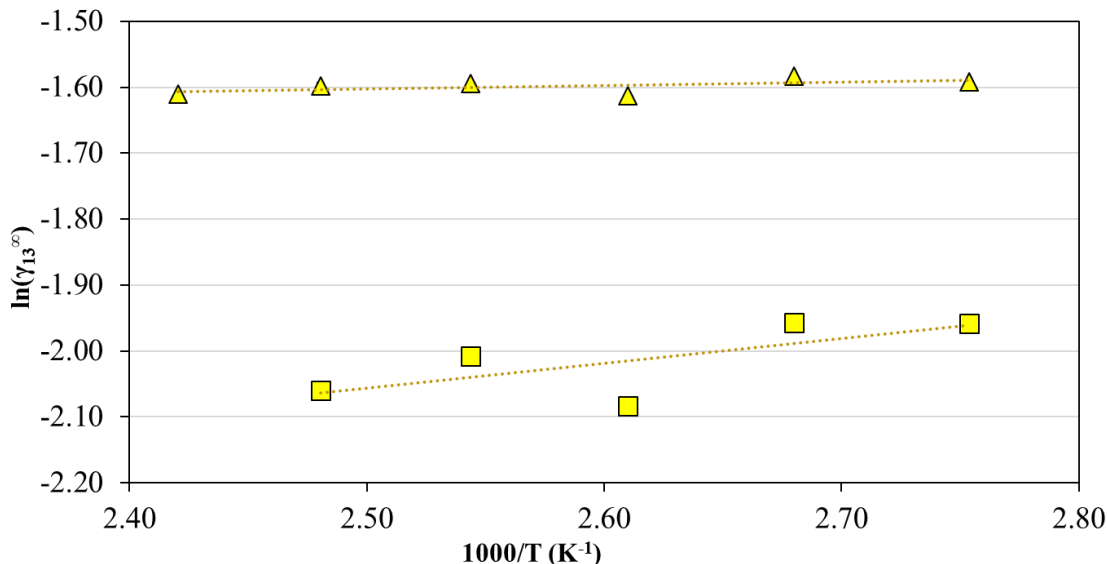


Figure 21 - $\ln(\gamma_{13}^{\infty})$ of water as a function of $1/T$ in Cyphos® IL 104 (\square) and in Cyphos® IL 101 (Δ).

As well as most other compounds, Cyphos® IL 104 presents greater interaction with water than Cyphos® IL 101. It is worth noting that the slope of the data changes from one IL to the other.

3.3.2. Partial excess energies

From the $\ln(\gamma_{13}^{\infty})$ data and its temperature dependence, it was possible to calculate the three partial excess energies ($\bar{G}_m^{E,\infty}$, $\bar{H}_m^{E,\infty}$ and $T\bar{S}_m^{E,\infty}$) which are shown in Figure 22 and Figure 23 and presented in Appendix C (Table C.3 to Table C.7).

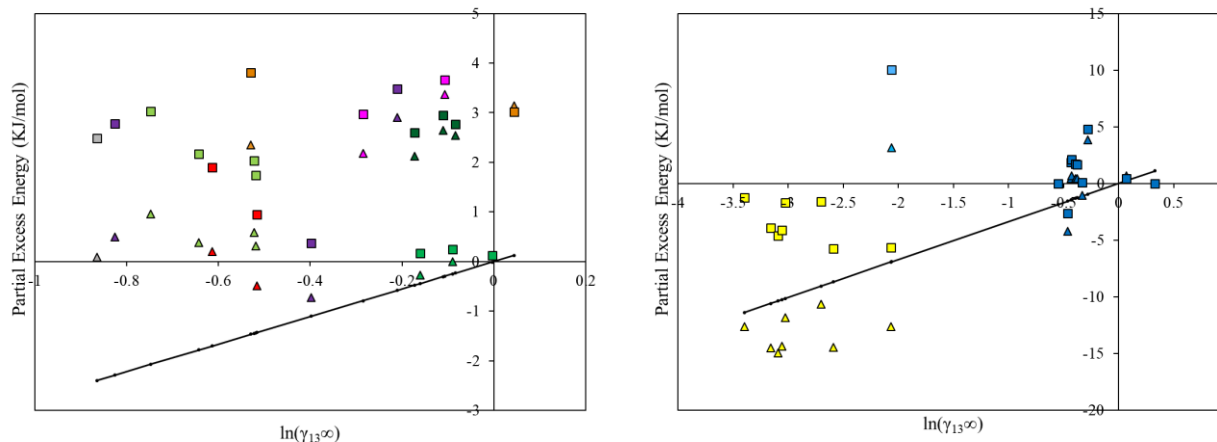


Figure 22- Partial molar excess energies as a function of the activity coefficients at infinite dilution of the solutes studied in the Cyphos® IL 104 in the left panel at 333.15 K and in the right panel at 403.15 K. The line represents $\bar{G}_m^{E,\infty}$, Δ represents $\bar{H}_m^{E,\infty}$ and \square represents $T\bar{S}_m^{E,\infty}$. Color code: \bullet alkanes; \bullet cycloalkanes; \bullet aromatic hydrocarbons; \bullet thiophene; \bullet ethers; \bullet ketones; \bullet esters; \bullet pyridine and acetonitrile; \bullet alcohols; \bullet water and \bullet terpenes.

In Cyphos® IL 104, it can be observed the difference between NP/NA solutes and AS solutes regarding entropic and enthalpic interactions. All alcohols present a highly negative enthalpic interaction when compared to the respective entropic interaction, while water and NP/NA solutes show mostly positive entropic and enthalpic interactions but being governed by the entropic effects. Additionally, terpenes showed no clear pattern of dominance between entropic and enthalpic effects, having mostly low values of partial excess energies. The lack of pattern can be due to the variety of functional groups present in different terpenoids.

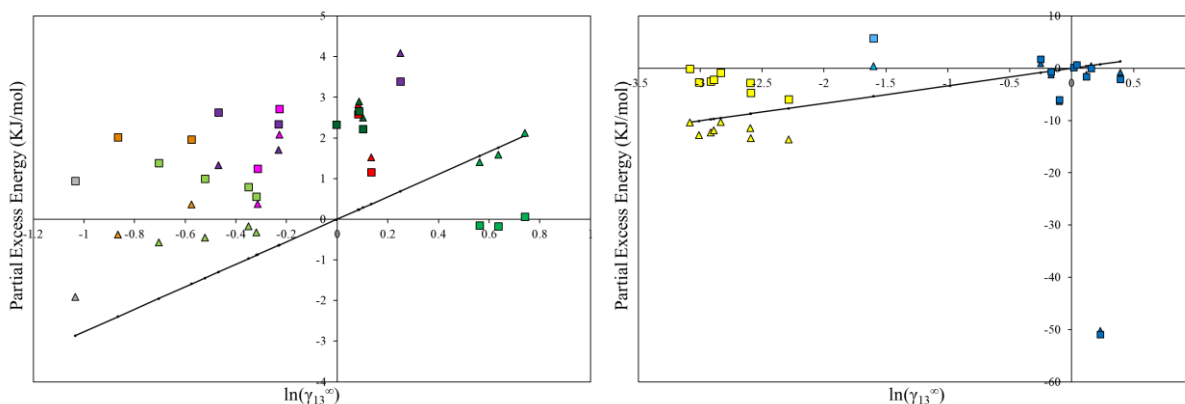


Figure 23 - Partial molar excess energies as a function of the activity coefficients at infinite dilution of the solutes studied in the Cyphos® IL 101 in the left panel at 333.15 K and in the right panel at 403.15 K. The line represents $\bar{G}_m^{E,\infty}$, Δ represents $\bar{H}_m^{E,\infty}$ and \square represents $T\bar{S}_m^{E,\infty}$. Color code: \bullet alkanes; \bullet cycloalkanes; \bullet aromatic hydrocarbons; \bullet thiophene; \bullet ethers; \bullet ketones; \bullet esters; \bullet pyridine and acetonitrile; \bullet alcohols; \bullet water and \bullet terpenes.

For Cyphos® IL 101, the same difference between NP/NA solutes and AS solutes can also be seen, however some changes were observed. The NP/NA solutes with positive $\ln(\gamma_{13}^{\infty})$ values showed higher enthalpic interactions while the ones with negative values, showed higher entropic interactions (except thiophene). Linalool showed strongly negative partial energies. Given the slope shown by linalool in Figure 20, it is expected a strongly negative $\bar{H}_m^{E,\infty}$, and, therefore, $T\bar{S}_m^{E,\infty}$. The differences in behavior between ILs of each group are also worth mentioning. Alkanes, cycloalkanes, thiophene and esters had a shift in the dominant effect between ILs, alongside the higher $\ln(\gamma_{13}^{\infty})$ values in Cyphos® IL 101 than in 104. Aromatic hydrocarbons and pyridine did not shift the energy dominance, however the enthalpic interaction between solutes and IL in Cyphos® IL 104 were positive, while in Cyphos® IL 101 are negative. The ethers presented unique differences, while two solutes (THF and 1,4-Dioxane) had little difference in the energy dominance, diethyl ether had a shift in dominant effect, as well as the increase in the $\ln(\gamma_{13}^{\infty})$ value. Ketones did not change in energy dominance although butanone had a decrease in both interactions

overall. While acetonitrile had a slight enthalpic dominant effect in Cyphos® IL 104, in Cyphos® IL 101 it showed the opposite, that is a stronger entropic effect. Alcohols maintained similar behavior in both ILs. Water remained with a stronger entropic interaction, while the terpenes in Figure 23 showed no clear dominant pattern either in Cyphos® IL 101 or in Cyphos® IL 104. Figure 24 shows data from all the terpenes tested in Cyphos® IL 101 at the same temperature.

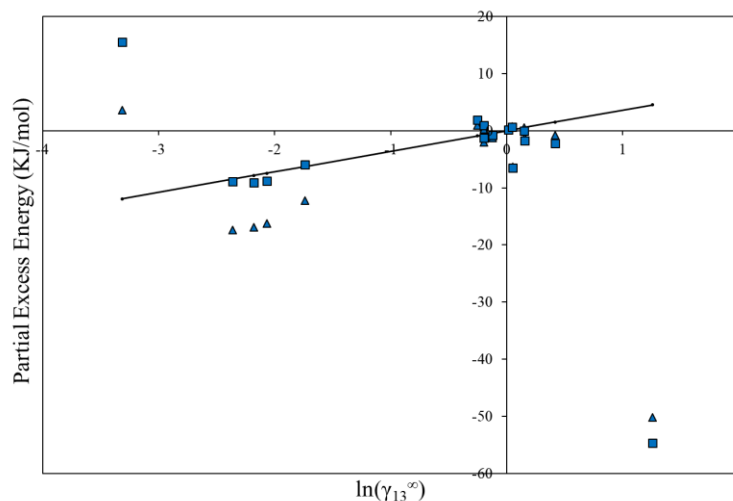


Figure 24 - Partial molar excess energies as a function of the activity coefficients at infinite dilution of the terpenes studied in the Cyphos® IL 101 at 433.15 K. The line represents $\bar{G}_m^{E,\infty}$, Δ represents $\bar{H}_m^{E,\infty}$ and \square represents $T\bar{S}_m^{E,\infty}$.

Most terpenes have comparatively low values of partial energies if compared to the other six compounds. The six compounds further away are all the alcoholic terpenoids in Figure 20, while most of them have dominant enthalpic effect, both borneol (the solute in the far left) and linalool (in the far right) show entropic dominance.

3.3.3. Capacity and selectivity

Regarding the capacities and selectivities, Figure 25 shows the results obtained relating some of the studied terpenes in both ILs.

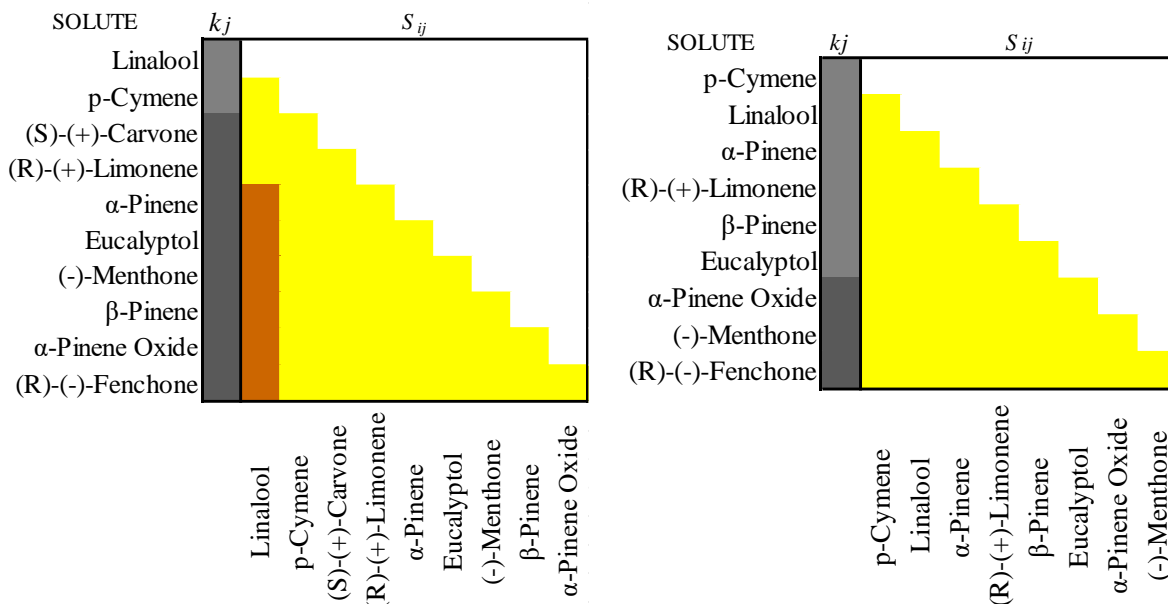


Figure 25 - S_{ij}^∞ and k_j^∞ of all terpenes and terpenoids at 403.15 K in Cyphos® IL 104 in the left panel and in Cyphos® IL 101 in the right panel. Color code: Selectivities, \color{yellow} [1-2] and \color{orange} [2-4]; Capacities, $\color{lightgray}$ <0.01; \color{gray} [0.01-0.05]; $\color{darkgray}$ [0.05-0.1]; \color{black} [0.1-0.2]; \color{black} [0.2-1] and \color{black} [1-2].

It can be observed moderate selectivity and capacity of Cyphos® IL 104 for limonene/linalool separation ($S_{ij}^\infty = 1.94$ and $k_j^\infty = 1.39$) while Cyphos® IL 101 achieved worse results ($S_{ij}^\infty = 1.12$ and $k_j^\infty = 0.89$). However, the α -pinene/ β -pinene selectivity was considerably low for both ILs ($S_{ij}^\infty = 1.06$ and in Cyphos® IL 104 and $S_{ij}^\infty = 1.12$ in Cyphos® IL 101) reaching moderate capacity in Cyphos® IL 104 ($k_j^\infty = 1.54$). The highest capacity determined using Cyphos® IL 104 at 403.15 K was for fenchone ($k_j^\infty = 1.73$) and the highest selectivity was for linalool/fenchone separation ($S_{ij}^\infty = 2.41$), while the lowest capacity was for linalool ($k_j^\infty = 0.72$) and the lowest selectivity was for menthone/ β -pinene separation ($S_{ij}^\infty = 1.00$). Although 403.15 K was enough to analyze all terpenes tested in Cyphos® IL 104, other terpenes were tested in Cyphos® IL 101 only at higher temperatures, therefore Figure 26 shows the results of all terpenes tested in Cyphos® IL 101.

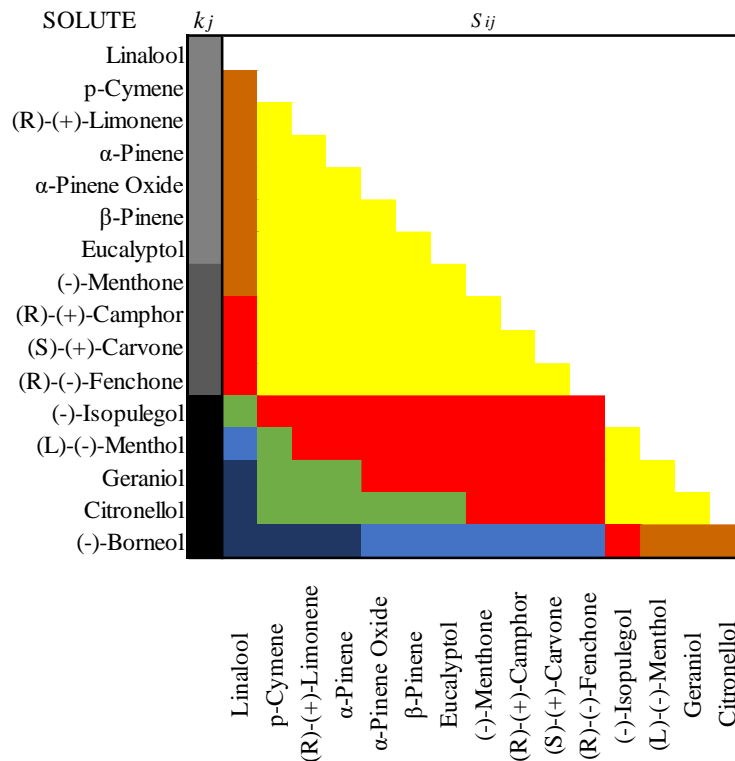


Figure 26 - S_{ij}^{∞} and k_j^{∞} of all terpenes and terpenoids at 433.15 K in Cyphos® IL 101. Color code: Selectivities, ● [1-2], ● [2-4], ● [4-10], ● [10-20], ● [20-30] and ● >30; Capacities, <0.01; ● [0.01-0.05]; ● [0.05-0.1]; ● [0.1-0.2]; ● [0.2-1], ● [1-2], ● [2-5] and ● >5.

At a higher temperature, Cyphos® IL 101 showed better results regarding the linalool/limonene separation although the poor capacity ($S_{ij}^{\infty} = 3.01$ and $k_j^{\infty} = 0.86$) while the α -pinene/ β -pinene separation data remained poor ($S_{ij}^{\infty} = 1.11$ and $k_j^{\infty} = 0.96$). The highest capacity determined using Cyphos® IL 101 at 433.15 K was for borneol ($k_j^{\infty} = 27.45$) and the highest selectivity was for linalool/borneol separation ($S_{ij}^{\infty} = 96.46$), while the lowest capacity was for linalool ($k_j^{\infty} = 0.29$) and the lowest selectivity was for carvone/camphor separation ($S_{ij}^{\infty} = 1.00$).

Table 3.2 presents the selectivities and capacities for α -pinene/ β -pinene separation, comparing solvents of previous works and the IL tested in the present work. Additionally, Figure 27 shows the same separation at different temperatures in the IL tested.

Table 3.2 - Selectivities (S_{ij}^{∞}) and capacities (k_j^{∞}) for the α -pinene/ β -pinene mixture at 403.15 K.

Solvent	Selectivities (S_{ij}^{∞})/ capacities (k_j^{∞})	Reference
Dinonyl Phthalate	1.26/1.15	[11] ^a
Amine 220	1.11/0.58	

Solvent	Selectivities (S_{ij}^{∞})/ capacities (k_j^{∞})	Reference
Tricresyl Phosphate	1.75/0.32	
Carbowax 6000	1.23/5.18	
Ethylene Glycol Phthalate	1.16/0.24	
Carbowax 1500	1.49/0.56	
[C ₄ mim] Cl	1.41/0.01	
[C ₄ mim] [CH ₃ SO ₃]	1.37/0.02	[1] ^b
[C ₄ mim] [(CH ₃) ₂ PO ₄]	1.27/0.04	
[C ₄ mim] [CF ₃ SO ₃]	1.32/0.05	
[P _{6,6,6,14}][(C ₈ H ₁₇) ₂ PO ₂]	1.06/1.54	This work
[P _{6,6,6,14}][Cl]	1.12/0.96	

^a Extrapolated value; ^b Interpolated value

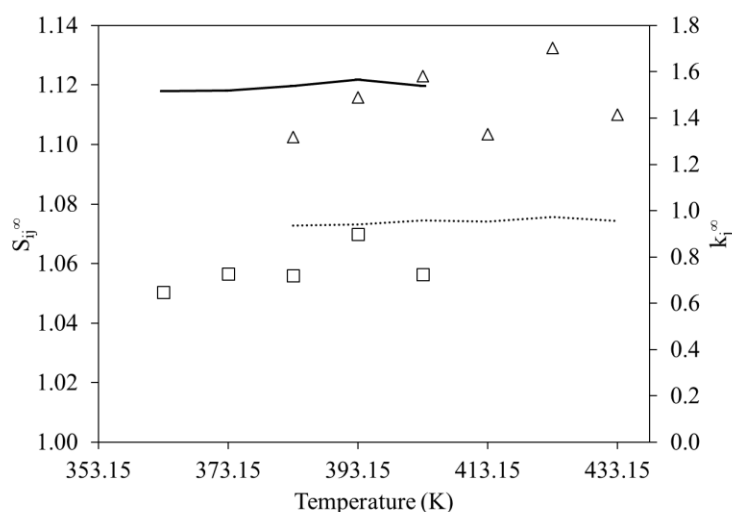


Figure 27 – Selectivities (S_{ij}^{∞}) and capacities (k_j^{∞}) of the α -pinene/ β -pinene separation at multiple temperatures. The \square represents the selectivity in Cyphos® IL 104, \triangle represents the selectivity in Cyphos® IL 101, the black line represents the capacity in Cyphos® IL 104 and the dotted line represents the capacity in Cyphos® IL 101.

Although the capacity achieved by Cyphos® IL 104 was comparatively high it also showed the lowest selectivity, while Cyphos® IL 101 had low selectivity and capacity. Although the capacities of the shown separations do not change much throughout the temperatures tested, a slightly positive slope can be noticed in the selectivity data for both ILs. Table 3.3 presents the selectivities and capacities for three separation problems (octane/benzene, cyclohexane/benzene and cyclohexane/thiophene) achieved using different ILs.

Table 3.3 - Selectivities (S_{ij}^{∞}) and capacities (k_j^{∞}) for different separation problems at 333.15 K

Ionic Liquid		Selectivities (S_{ij}^{∞})/ capacities (k_j^{∞})			Reference
Cation	Anion	Octane /Benzene	Cyclohexane /Benzene	Cyclohexane /Thiophene	
[Hmim] ⁺	[BF ₄] ⁻	30.32/1.06	10.04/1.06	---	[41] ^a
	[FAP] ⁻	19.10/1.84	7.61/1.84	6.97/1.68	[42] ^b
[C ₁ mim] ⁺	[MeSO ₄] ⁻	---	14.94/0.17	---	[43]
	[CH ₃ OC ₂ H ₄ SO ₄] ⁻	---	23.98/0.24	---	[43]
	[Me ₂ PO ₄] ⁻	84.15/0.27	12.02/0.27	---	[43]
[C ₂ mim] ⁺	[MeSO ₃] ⁻	50.44/0.24	18.08/0.24	39.21/0.51	[42] ^b
	[DEP] ⁻	52.48/0.42	12.59/0.42	---	[44]
[C ₄ mim] ⁺	[CF ₃ SO ₃] ⁻	36.87/0.62	9.79/0.62	13.43/0.86	[45] ^b
	[DCA] ⁻	63.15/0.50	12.38/0.50	19.7/0.8	[46] ^b
	[BETI] ⁻	18.45/0.98	6.41/0.98	6.67/1.02	[42] ^b
	[DBP] ⁻	6.84/1.08	3.05/1.08	---	[47]
	Cl ⁻	99.85/0.24	15.74/0.24	38.16/0.57	[1] ^a
	[MeSO ₃] ⁻	68.18/0.36	13.29/0.36	25.43/0.70	[1] ^a
[C ₈ mim] ⁺	[(CH ₃) ₂ PO ₄] ⁻	25.35/0.48	6.35/0.48	12.97/0.99	[1] ^a
	Cl ⁻	13.40/0.63	5.58/0.63	---	[48] ^b
[C ₄ mPyr] ⁺	[TCM] ⁻	41.02/0.95	9.73/0.95	13.84/1.35	[49]
[Hpy] ⁺	[C ₂ H ₅ OC ₂ H ₄ SO ₄] ⁻	37.23/0.27	7.82/0.27	---	[43] ^b
[C ₂ py] ⁺	[BTI] ⁻	43.57/0.71	10.50/0.71	---	[43]
[P _{1,4,4,4}] ⁺	[MeSO ₄] ⁻	14.80/1.12	5.09/1.12	---	[50] ^a
	[TPTP] ⁻	4.05/5.37	2.33/5.37	---	[40] ^a
	[C(CN) ₃] ⁻	5.01/2.13	2.44/2.13	2.73/2.38	[51] ^b
	Cl ⁻	2.05/2.51	1.57/2.51	---	[3] ^a
	Cl ⁻	3.55/2.02	2.20/2.02	3.05/2.81	This work
	[BF ₄] ⁻	2.95/2.74	1.94/2.74	---	[3] ^a
	[(Tf) ₂ N] ⁻	2.01/2.5	1.51/2.50	---	[3] ^a
	[(C ₈ H ₁₇) ₂ PO ₂] ⁻	1.70/1.81	1.10/1.81	---	[4] ^a
[P _{6,6,6,14}] ⁺	[(C ₈ H ₁₇) ₂ PO ₂] ⁻	1.80/2.11	1.14/2.11	1.29/2.37	This work

^a Extrapolated value; ^b Interpolated value

Comparatively, the capacities acquired for both ILs were high, however both showed one of the lowest selectivities, which discourage them as a separation agent for all the separation problems shown in Table 3.3. It is also relevant to point out the high similarity of the results found in this work and those published in an independent work [3,4].

There are few data regarding the limonene/linalool separation and, among those, none use the method in the present work. As mentioned earlier, fewer data could be acquired in Cyphos® IL 104 for limonene and linalool (3 and 1 temperatures, respectively). Figure 28 shows the selectivities and capacities of that data and the ones gathered in Cyphos® IL 101.

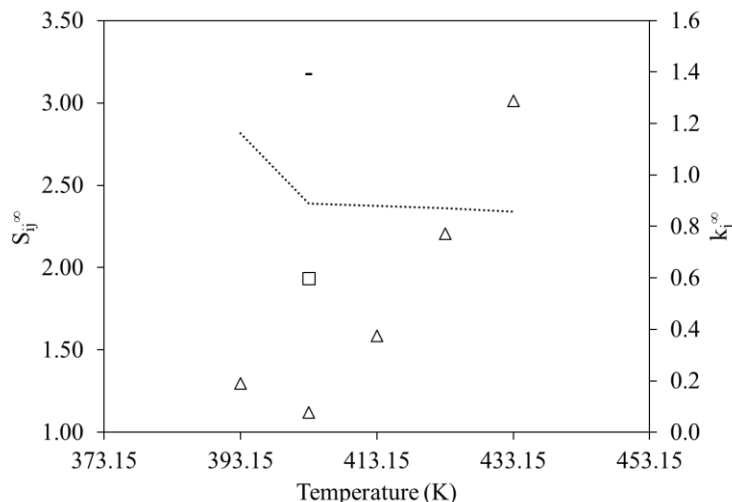


Figure 28 - Selectivities (S_{ij}^{∞}) and capacities (k_j^{∞}) of the limonene/linalool separation at multiple temperatures. The \square represents the selectivity in Cyphos® IL 104, \triangle represents the selectivity in Cyphos® IL 101, the black dot represents the capacity in Cyphos® IL 104 and the dotted line represents the capacity in Cyphos® IL 101.

Since linalool presented a highly negative slope, as shown in Figure 20, it is expected a highly variable selectivity. At 403.15 K the selectivity in Cyphos® IL 104 and Cyphos® IL 101 were, respectively, 1.94 and 1.12, while the capacities were 1.39 and 0.89. The highest selectivity value was achieved at 433.15 K in Cyphos® IL 101, reaching 3.01, while the capacity was 0.86 at that temperature. The higher selectivity and capacity of Cyphos® IL 104 over Cyphos® IL 101 at one of the lowest possible temperatures confirms the predictions of COSMO-RS made by Martins [1].

3.3.4. Gas-liquid partition coefficient

Following Equation 11, it was possible to calculate the gas-liquid partition coefficient for all solutes and are presented in Appendix C (Table C.8 and Table C.9). However, since this property is temperature-dependent and in order to present a succinct graphic, Figure 29 shows K_L data acquired in the median temperature as well as the number of carbon atoms in each solute.

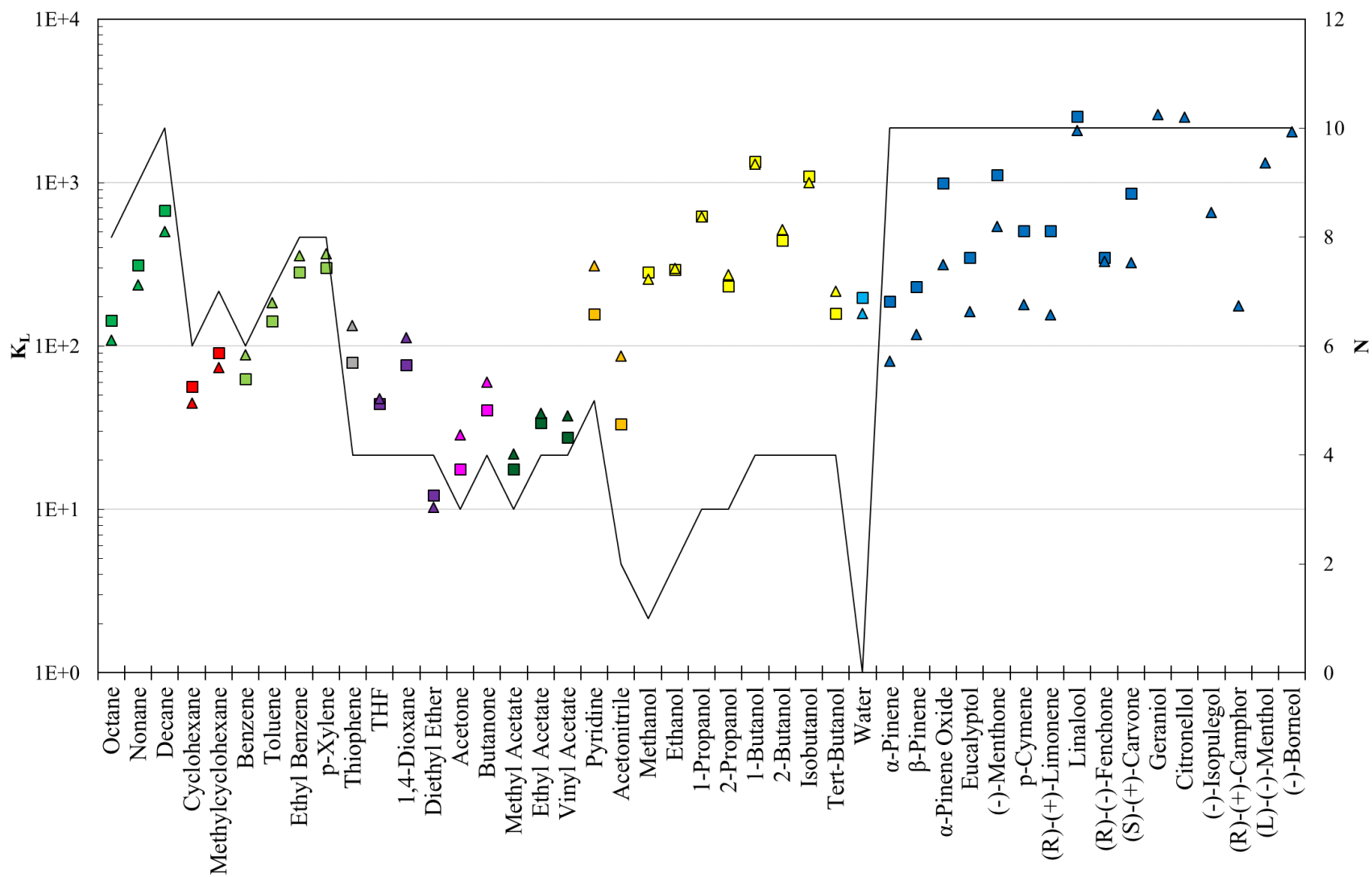


Figure 29 – Gas-liquid partition coefficients of the solutes studied in Cyphos® IL 104 (\square) and in Cyphos® IL 101 (\triangle) at median temperature. The line represents the number of carbons N . Color code: ● alkanes; ● cycloalkanes; ● aromatic hydrocarbons; ● thiophene; ● ethers; ● ketones; ● esters; ● pyridine and acetonitrile; ● alcohols; ● water and ● terpenes.

The Figure 29 shows that for aromatic hydrocarbons, thiophene, most ethers, ketone, esters, acetonitrile, pyridine and some alcohols, the K_L value is higher in Cyphos® IL 101 than in Cyphos® IL 104. Meanwhile, alkanes, cycloalkanes, some alcohols, water and terpenes have higher K_L values in Cyphos® IL 104 than in Cyphos® IL 101. It can be noticed that in the alkanes, cycloalkanes, aromatic hydrocarbons, ketones and esters the carbon count has great relevancy, increasing the K_L increasing the number of carbon atoms in the molecule. Additionally, the correlation between the K_L value and the carbon number for the groups before mentioned is almost linear. The alcohols also show a correlation between K_L and number of carbon atoms when viewing the alcohol sub-groups individually. Thiophene, ethers, acetonitrile and pyridine had no clear pattern regarding the number of carbon atoms. In order to evaluate the terpenes tested Figure 30 shows the terpenes grouped by their functional group.

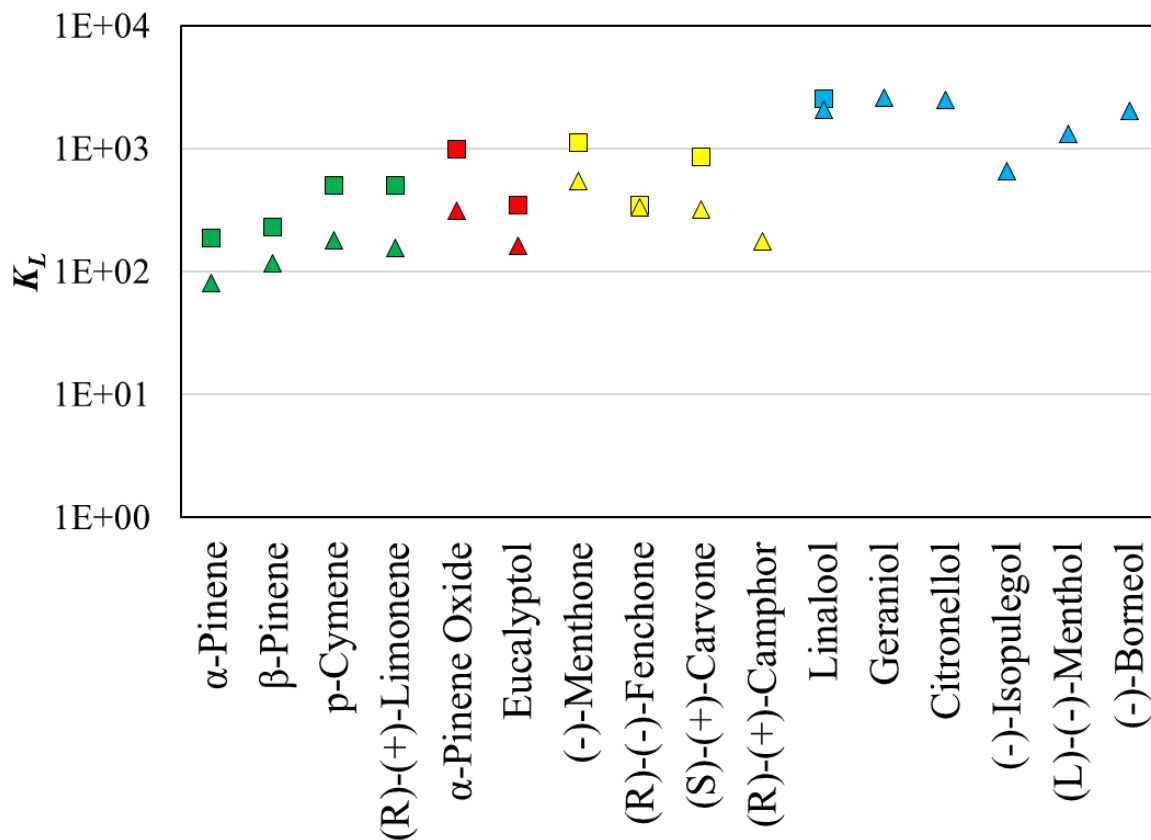


Figure 30 – Gas-liquid partition coefficients of the terpenes studied in Cyphos® IL 104 (\square) and in Cyphos® IL 101 (\triangle) at median temperature. Color code: ● alkanes; ● ether; ● ketone and ● alcohol.

Unlike most groups presented in Figure 29, no clear pattern can be noticed in the terpenes, not even when grouped by their functional group.

3.3.5. Relevancy of each term on the IDAC equation

As shown before, the equation which calculated the activity coefficient at infinite dilution has three parts, as shown in Figure 31, however it was still unclear which of those is more relevant or impactful in the γ_{13}^{∞} value.

$$\ln(\gamma_{13}^{\infty}) = \underbrace{\ln\left(\frac{n_3 RT}{V_N P_1^*}\right)}_{1^{\text{st}} \text{ term}} - \underbrace{\frac{P_1^*(B_{111} - V_1^*)}{RT}}_{2^{\text{nd}} \text{ term}} + \underbrace{\frac{P_o J_2^3 (2B_{112} - V_1^{\infty})}{RT}}_{3^{\text{rd}} \text{ term}}$$

Figure 31 – Partition used on A.C.I.D Equation.

In order to evaluate and compare that importance, all data used to calculate γ_{13}^{∞} values were also used to calculate the value of each part individually. Figure 32 and Figure 33 show all the data of each part of the IDAC equation either in Cyphos® IL 104 or Cyphos® IL 101, respectively.

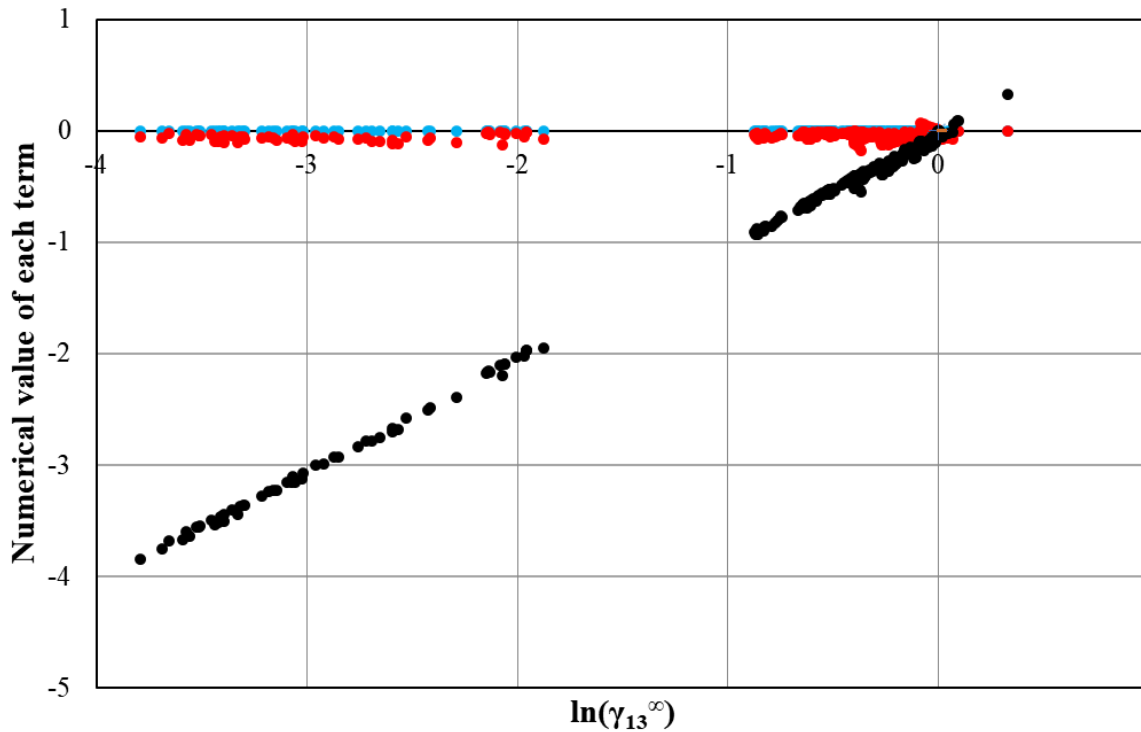


Figure 32 – Value of each part of the IDAC. equation in function of its respective $\ln(\gamma_{13}^{\infty})$ in Cyphos® IL 104. Color code: ● 1st part; ● 2nd part and ● 3rd part.

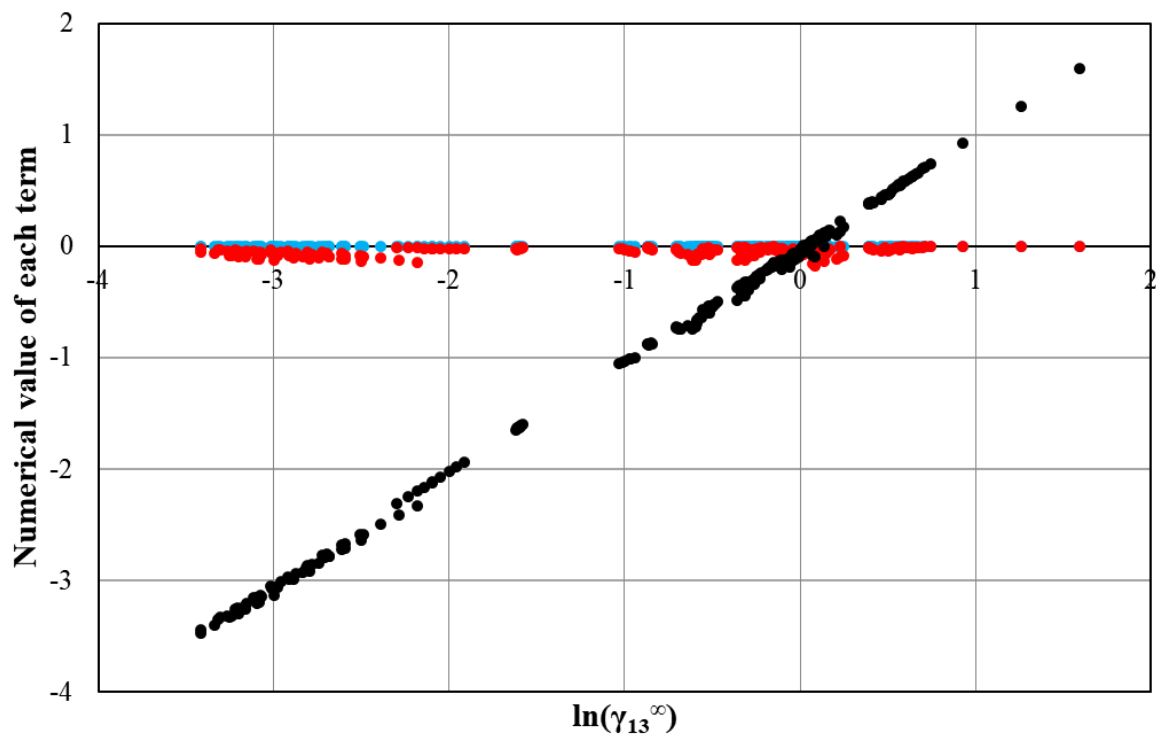


Figure 33 – Value of each part of the A.C.I.D. equation in function of its respective $\ln(\gamma_{13}^{\infty})$ in Cyphos® IL 101. Color code: ● 1st part; ● 2nd part and ● 3rd part.

It is clear the almost linear correlation between the data calculated using the first part and the $\ln(\gamma_{13}^{\infty})$, while the second and third parts stay at much substantially low values. It can be implied that the first part is the most relevant between the three components to calculate the γ_{13}^{∞} value.

Chapter 4. Conclusions and future work

Experimental data on activity coefficients at infinite dilution of different solutes in the Cyphos® IL 104 and Cyphos® IL 101 were measured by gas chromatography technique for diverse organic solutes, water and terpenes, at different temperatures. After analyzing the data, a different behavior was observed between solutes that can establish hydrogen bonds and those which cannot. Additionally, among solutes not able of hydrogen bonding, a small difference was observed between less polar solutes and more polar ones. Some changes of behavior were observed by the same solute when tested in the different ILs, showing the relevancy of the different anions. Regarding the infinite dilution excess partial properties, significant differences are observed among the studied organic solutes in both ILs. For alcohols and some terpenoids, the enthalpic behavior is dominant, whereas the entropic effects are dominant in hydrocarbons and less polar solutes.

Regarding the performance as separation agents of terpenes, the studied ILs had questionable suitability to separate both limonene/linalool and α -pinene/ β -pinene mixtures, once no satisfactory capacities and/or selectivities were found for both separation problems in both ILs. Other separation problems present in petrochemical industry showed more promising results in Cyphos® 101.

Regarding the gas-liquid partition coefficients, in both ILs it was showed, for most functional groups, good correlations between that coefficient and the number of carbon present in the solute. However, terpenes showed no clear pattern. It was also noticed that the equation used to calculate the activity coefficients has its first component as the most relevant.

In addition, the main results of this work were summarized alongside other results in a paper accepted to be published (in Oct 20, 2020) on the Journal of Molecular Liquids.

Future work might include further studies using ionic liquids containing $[P_{6,6,6,14}]^+$ cation with different anions, maintaining $[(C_8H_{17})_2PO_2]^-$ or $[Cl]^-$ anions, with other cations, or possibly more interestingly a mixture of two ILs that possess the same cation, which can give more hints about the relevancy of the cation, or the anion of an IL. Besides, COSMO-RS can also be applied to predict the activity coefficients of the studied ILs, to test its predictive character and, later, be used to select new ionic liquids, their mixtures or even eutectic mixtures to target the separation problems studied in the present work.

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Appendix A. Calculation of the pressure drop at outlet column conditions

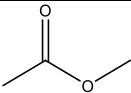
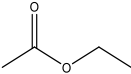
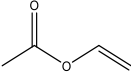

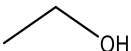
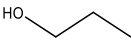

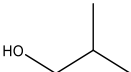
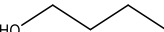
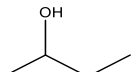
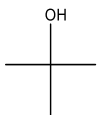
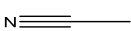
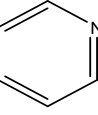
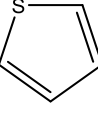
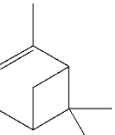
Table A.1 – Coefficients of equation 5 at different temperatures.

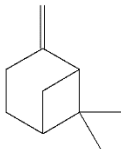
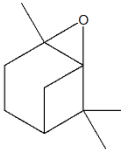
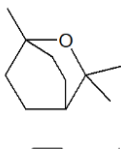
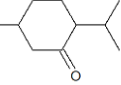
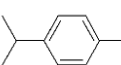
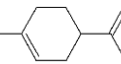
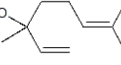
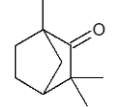
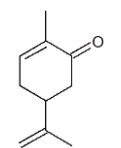
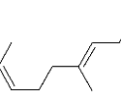
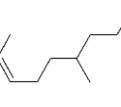
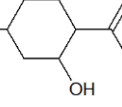
Temperature (°C)	25	30	35	40	45	50	55	60
<i>A</i>	0.1069	0.0724	0.1407	0.1641	0.0891	0.3358	0.4718	0.2722
<i>B</i>	0.0264	0.0261	0.0253	0.0245	0.0257	0.0285	0.0243	0.0274
<i>R</i> ²	0.9998	0.9997	0.9999	0.9989	0.9999	0.9927	0.9997	0.9998
Temperature (°C)	65	70	75	80	85	90	95	100
<i>A</i>	0.2818	0.3327	0.3067	0.2734	0.2786	0.2843	0.2861	0.2861
<i>B</i>	0.0270	0.0261	0.0258	0.0259	0.0255	0.0252	0.0249	0.0249
<i>R</i> ²	0.9999	0.9996	0.9999	0.9993	0.9999	1.0000	1.0000	1.0000
Temperature (°C)	105	110	115	120	125	130	135	140
<i>A</i>	0.2626	0.2373	0.2145	0.2140	0.1926	0.1712	0.2124	0.2082
<i>B</i>	0.0248	0.0251	0.0254	0.0252	0.0253	0.0255	0.0249	0.0249
<i>R</i> ²	0.9998	0.9992	1.0000	1.0000	0.9999	0.9996	0.9991	0.9991
Temperature (°C)	145	150	155	160	165	170	175	180
<i>A</i>	0.2082	0.2082	0.2082	0.2082	0.2082	0.2082	0.2082	0.2082
<i>B</i>	0.0249	0.0249	0.0249	0.0249	0.0249	0.0249	0.0249	0.0249
<i>R</i> ²	0.9991	0.9991	0.9991	0.9991	0.9991	0.9991	0.9991	0.9991

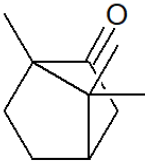
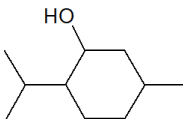
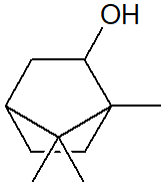
Appendix B. List of solutes

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 purity ^a
Alkanes	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	≥ 0.999
	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
	<i>p</i> -Xylene		Aldrich	≥ 0.990

	Chemicals		Source	Mass fraction purity ^a
Esters	Methyl acetate		Aldrich	≥ 0.998
	Ethyl acetate		Aldrich	≥ 0.998
	Vinyl acetate		Aldrich	≥ 0.990
Alcohols	Methanol		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 (<i>tert</i> - Butanol)		Aldrich	≥ 0.997
	Acetonitrile		Fluka	≥ 0.999
Pyridine		Aldrich	≥ 0.998	
Thiophene		Aldrich	≥ 0.990	
Water	H ₂ O			
Terpenes/ Terpenoids	α -Pinene		Sigma- Aldrich	0.980

Chemicals		Source	Mass fraction purity ^a
β -Pinene		Sigma-Aldrich	0.990
α -Pinene Oxide		Aldrich	0.970
Eucalyptol		Aldrich	0.990
(-)-Menthone		Fluka	≥ 0.990
p-Cymmene		Aldrich	0.990
(R)-(+)-Limonene		Aldrich	0.970
Linalool		Aldrich	0.970
(R)-(-)-Fenchone		Aldrich	≥ 0.980
(S)-(+)-Carvone		Merck	0.960
Geraniol		Aldrich	≥ 0.980
Citronellol		Aldrich	≈ 0.950
(-)-Isopulegol		SAFC	≥ 0.980

Chemicals		Source	Mass fraction purity ^a
(R)-(+)-Camphor		Aldrich	≥ 0.980
(L)-(-)-Menthol		Acros	≥ 0.997
(-)-Borneol		Fluka	≥ 0.990

^aDeclared by the supplier.

Appendix C. Physicochemical properties

Table C.1 – Activity Coefficients at Infinite Dilution in Cyphos® IL 104.

Solute	Temperature (K)					
	333.15	343.15	353.15	363.15	373.15	383.15
Octane	0.851	0.851	0.855	0.853	0.867	0.858
Nonane	0.914	0.918	0.919	0.921	0.923	0.910
Decane	0.997	0.997	0.996	0.998	1.001	0.986
Cyclohexane	0.542	0.544	0.537	0.536	0.542	0.536
Methylcyclohexane	0.597	0.586	0.585	0.608	0.611	0.597
Benzene	0.474	0.474	0.471	0.466	0.460	0.454
Toluene	0.526	0.524	0.526	0.520	0.526	0.513
Ethyl Benzene	0.593	0.591	0.597	0.587	0.588	0.574
p-Xylene	0.596	0.597	0.607	0.596	0.597	0.585
Thiophene	0.421	0.422	0.421	0.417	0.424	0.419
THF	0.438	0.440	0.436	0.432	0.436	0.427
1,4-Dioxane	0.810	0.787	0.765	0.745	0.732	0.702
Diethyl Ether	0.671	0.670	0.671	0.682	0.689	0.691
Acetone	0.899	0.868	0.836	0.810	0.793	0.766
Butanone	0.752	0.738	0.724	0.707	0.700	0.675
Methyl Acetate	0.895	0.864	0.839	0.818	0.805	0.789
Ethyl Acetate	0.842	0.821	0.803	0.788	0.781	0.757
Vinyl Acetate	0.920	0.894	0.865	0.843	0.832	0.817
Pyridine	0.589	0.576	0.563	0.555	0.543	0.524
Acetonitrile	1.046	1.018	0.985	0.954	0.934	0.901

Solute	Temperature (K)					
	363.15	373.15	383.15	393.15	403.15	413.15
Methanol	0.023	0.025	0.028	0.032	0.034	---
Ethanol	0.034	0.037	0.040	0.046	0.049	---
1-Propanol	0.030	0.033	0.037	0.043	0.047	---
2-Propanol	0.049	0.054	0.058	0.068	0.067	---
1-Butanol	0.028	0.032	0.035	0.042	0.045	---
2-Butanol	0.047	0.052	0.057	0.066	0.075	---
Isobutanol	0.026	0.030	0.030	0.036	0.042	---
Tert-Butanol	0.080	0.089	0.089	0.102	0.126	---
Water	0.141	0.141	0.124	0.134	0.127	---
α -Pinene	0.693	0.695	0.686	0.683	0.687	---
β -Pinene	0.660	0.658	0.650	0.638	0.650	0.652
α -Pinene Oxide	0.550	0.567	---	---	0.630	---
Eucalyptol	0.671	0.673	---	---	0.675	0.654
(-)-Menthone	0.673	0.669	---	---	0.652	0.658
p-Cymene	1.095	1.100	---	---	1.074	---
(R)-(+)-Limonene	0.695	0.700	---	---	0.719	---
Linalool	---	---	---	---	1.391	---
(R)-(-)-Fenchone	---	---	---	---	0.576	---
(S)-(+)-Carvone	---	---	---	---	0.756	0.735

Table C.2 – Activity Coefficients at Infinite Dilution in Cyphos® IL 101.

Solute	Temperature (K)								
	333.15	343.15	353.15	363.15	373.15	383.15	393.15	403.15	413.15
Octane	1.755	1.733	1.698	1.670	1.658	1.649	---	---	---
Nonane	1.891	1.857	1.825	1.773	1.770	1.764	---	---	---
Decane	2.098	2.032	2.013	1.955	1.931	1.892	---	---	---
Cyclohexane	1.087	1.048	1.032	0.977	0.992	0.943	---	---	---
Methylcyclohexane	1.144	1.115	1.105	1.075	1.076	1.064	---	---	---
Benzene	0.494	0.493	0.497	0.500	0.501	0.508	---	---	---
Toluene	0.593	0.595	0.599	0.607	0.605	0.603	---	---	---
Ethyl Benzene	0.705	0.704	0.698	0.707	0.706	0.711	---	---	---
p-Xylene	0.727	0.731	0.732	0.740	0.733	0.740	---	---	---
Thiophene	0.356	0.362	0.369	0.378	0.381	0.390	---	---	---
THF	0.626	0.617	0.610	0.598	0.585	0.595	---	---	---
1,4-Dioxane	0.794	0.782	0.769	0.757	0.736	0.738	---	---	---
Diethyl Ether	1.283	1.254	1.235	1.145	1.076	1.091	---	---	---
Acetone	0.795	0.774	0.768	0.744	0.719	0.729	---	---	---
Butanone	0.730	0.720	0.721	0.716	0.720	0.714	---	---	---
Methyl Acetate	1.090	0.991	1.021	0.975	0.939	0.941	---	---	---
Ethyl Acetate	1.108	1.071	1.050	1.019	0.987	0.993	---	---	---
Vinyl Acetate	0.997	0.963	0.948	0.923	0.896	0.899	---	---	---
Pyridine	0.421	0.419	0.420	0.427	0.421	0.429	---	---	---
Acetonitrile	0.563	0.556	0.556	0.554	0.550	0.553	---	---	---
Methanol	---	---	---	0.033	0.036	0.039	0.042	0.046	0.050
Ethanol	---	---	---	0.043	0.046	0.050	0.054	0.059	0.065
1-Propanol	---	---	---	0.038	0.041	0.046	0.051	0.056	0.061
2-Propanol	---	---	---	0.052	0.056	0.062	0.068	0.075	0.082
1-Butanol	---	---	---	0.037	0.040	0.044	0.049	0.054	0.060
2-Butanol	---	---	---	0.049	0.054	0.060	0.067	0.075	0.083
Isobutanol	---	---	---	0.033	0.036	0.041	0.045	0.049	0.055
Tert-Butanol	---	---	---	0.066	0.074	0.081	0.092	0.102	0.113
Water	---	---	---	0.204	0.205	0.199	0.203	0.202	0.200

Solute	Temperature (K)										
	383.15	393.15	403.15	413.15	423.15	433.15	438.15	443.15	448.15	453.15	458.15
α -Pinene	1.177	1.185	1.171	1.157	1.164	1.161	---	---	---	---	---
β -Pinene	1.068	1.062	1.043	1.048	1.028	1.046	---	---	---	---	---
α -Pinene Oxide	0.832	0.894	0.905	0.963	1.009	1.053	---	---	---	---	---
Eucalyptol	1.021	1.031	1.016	1.018	1.022	1.016	---	---	---	---	---
(-)-Menthone	0.853	0.847	0.848	0.863	0.881	0.885	---	---	---	---	---
p-Cymene	1.482	1.476	1.483	1.489	1.512	1.518	---	---	---	---	---
(R)-(+)-Limonene	1.118	1.118	1.124	1.137	1.148	1.166	---	---	---	---	---
Linalool	---	0.861	1.259	1.803	2.532	3.514	---	4.911	---	---	---
(R)-(-)-Fenchone	0.798	0.794	0.780	0.786	0.766	0.776	---	---	---	---	---
(S)-(+)-Carvone	---	---	---	---	---	0.822	0.845	0.849	0.850	0.833	0.865
Geraniol	---	---	---	---	---	0.113	0.123	0.129	0.135	0.141	0.148
Citronellol	---	---	---	---	---	0.094	0.101	0.107	0.113	0.118	0.123
(-)-Isopulegol	---	---	---	---	---	0.176	0.183	0.191	0.200	0.201	0.214
(R)-(+)-Camphor	---	---	---	---	---	0.822	0.818	0.816	0.806	0.839	0.808
(L)-(-)-Menthol	---	---	---	---	---	0.127	0.135	0.143	0.149	0.154	0.163
(-)-Borneol	---	---	---	---	---	0.036	0.036	0.036	0.035	0.035	0.035

Table C.3 – Partial Excess Gibbs’ Free Energy at Infinite Dilution ($\bar{G}_m^{E,\infty}$) in Cyphos® IL 104.

Solute	Temperature (K)					
	333.15	343.15	353.15	363.15	373.15	383.15
Octane	-0.446	-0.462	-0.459	-0.482	-0.441	-0.489
Nonane	-0.250	-0.245	-0.249	-0.249	-0.248	-0.301
Decane	-0.009	-0.010	-0.013	-0.007	0.002	-0.046
Cyclohexane	-1.699	-1.736	-1.825	-1.882	-1.901	-1.985
Methylcyclohexane	-1.430	-1.522	-1.572	-1.504	-1.531	-1.643
Benzene	-2.070	-2.127	-2.212	-2.307	-2.408	-2.519
Toluene	-1.779	-1.842	-1.885	-1.976	-1.995	-2.126
Ethyl Benzene	-1.446	-1.499	-1.517	-1.607	-1.650	-1.767
p-Xylene	-1.436	-1.474	-1.464	-1.561	-1.600	-1.710
Thiophene	-2.395	-2.462	-2.537	-2.639	-2.664	-2.775
THF	-2.289	-2.345	-2.436	-2.536	-2.578	-2.713
1,4-Dioxane	-0.584	-0.683	-0.785	-0.890	-0.968	-1.125
Diethyl Ether	-1.104	-1.142	-1.172	-1.156	-1.155	-1.179
Acetone	-0.295	-0.405	-0.528	-0.638	-0.720	-0.851
Butanone	-0.790	-0.866	-0.950	-1.048	-1.107	-1.251
Methyl Acetate	-0.307	-0.417	-0.515	-0.607	-0.673	-0.753
Ethyl Acetate	-0.477	-0.562	-0.645	-0.718	-0.768	-0.886
Vinyl Acetate	-0.232	-0.320	-0.426	-0.516	-0.570	-0.644
Pyridine	-1.466	-1.575	-1.685	-1.776	-1.897	-2.058
Acetonitrile	0.124	0.051	-0.044	-0.142	-0.211	-0.333

Solute	Temperature					
	363.15	373.15	383.15	393.15	403.15	413.15
Methanol	-11.438	-11.441	-11.441	-11.238	-11.377	---
Ethanol	-10.253	-10.235	-10.233	-10.036	-10.139	---
1-Propanol	-10.606	-10.577	-10.492	-10.269	-10.242	---
2-Propanol	-9.113	-9.065	-9.077	-8.783	-9.047	---
1-Butanol	-10.781	-10.721	-10.685	-10.401	-10.365	---
2-Butanol	-9.260	-9.176	-9.149	-8.888	-8.686	---
Isobutanol	-11.034	-10.927	-11.167	-10.840	-10.587	---
Tert-Butanol	-7.631	-7.494	-7.718	-7.475	-6.935	---
Water	-5.912	-6.073	-6.639	-6.565	-6.907	---
α -Pinene	-1.107	-1.129	-1.200	-1.246	-1.259	---
β -Pinene	-1.256	-1.300	-1.374	-1.467	-1.443	-1.470
α -Pinene Oxide	-1.807	-1.762	---	---	-1.550	---
Eucalyptol	-1.206	-1.230	---	---	-1.320	-1.459
(-)-Menthone	-1.196	-1.247	---	---	-1.433	-1.436
p-Cymene	0.274	0.295	---	---	0.240	---
(R)-(+)-Limonene	-1.099	-1.106	---	---	-1.108	---
Linalool	---	---	---	---	1.106	---
(R)-(-)-Fenchone	---	---	---	---	-1.847	---
(S)-(+)-Carvone	---	---	---	---	-0.937	-1.056

Table C.4 – Partial Excess Gibbs’ Free Energy at Infinite Dilution ($\bar{G}_m^{E,\infty}$) in Cyphos® IL 101.

Solute	Temperature (K)								
	333.15	343.15	353.15	363.15	373.15	383.15	393.15	403.15	413.15
Octane	1.558	1.569	1.554	1.548	1.569	1.593	---	---	---
Nonane	1.764	1.766	1.767	1.729	1.772	1.808	---	---	---
Decane	2.052	2.022	2.055	2.023	2.042	2.031	---	---	---
Cyclohexane	0.230	0.134	0.093	-0.070	-0.026	-0.185	---	---	---
Methylcyclohexane	0.373	0.311	0.294	0.218	0.228	0.196	---	---	---
Benzene	-1.952	-2.016	-2.054	-2.092	-2.146	-2.157	---	---	---
Toluene	-1.446	-1.480	-1.507	-1.506	-1.560	-1.610	---	---	---
Ethyl Benzene	-0.969	-1.000	-1.056	-1.045	-1.082	-1.088	---	---	---
p-Xylene	-0.882	-0.893	-0.916	-0.909	-0.962	-0.960	---	---	---
Thiophene	-2.863	-2.898	-2.930	-2.939	-2.996	-3.002	---	---	---
THF	-1.298	-1.377	-1.450	-1.553	-1.665	-1.654	---	---	---
1,4-Dioxane	-0.640	-0.701	-0.769	-0.842	-0.949	-0.967	---	---	---
Diethyl Ether	0.691	0.646	0.620	0.409	0.227	0.277	---	---	---
Acetone	-0.635	-0.732	-0.775	-0.892	-1.022	-1.005	---	---	---
Butanone	-0.870	-0.936	-0.959	-1.009	-1.018	-1.072	---	---	---
Methyl Acetate	0.240	-0.025	0.061	-0.077	-0.196	-0.195	---	---	---
Ethyl Acetate	0.284	0.195	0.144	0.057	-0.040	-0.023	---	---	---
Vinyl Acetate	-0.010	-0.107	-0.156	-0.241	-0.340	-0.341	---	---	---
Pyridine	-2.397	-2.481	-2.544	-2.567	-2.683	-2.696	---	---	---
Acetonitrile	-1.593	-1.673	-1.726	-1.783	-1.852	-1.886	---	---	---
Methanol	---	---	---	-10.315	-10.348	-10.327	-10.338	-10.332	-10.306
Ethanol	---	---	---	-9.531	-9.546	-9.534	-9.517	-9.496	-9.413
1-Propanol	---	---	---	-9.869	-9.878	-9.782	-9.731	-9.683	-9.610
2-Propanol	---	---	---	-8.932	-8.922	-8.863	-8.783	-8.702	-8.591
1-Butanol	---	---	---	-9.973	-9.986	-9.922	-9.843	-9.774	-9.669
2-Butanol	---	---	---	-9.113	-9.054	-8.948	-8.818	-8.690	-8.538
Isobutanol	---	---	---	-10.311	-10.296	-10.212	-10.148	-10.083	-9.972
Tert-Butanol	---	---	---	-8.229	-8.097	-7.994	-7.817	-7.656	-7.495
Water	---	---	---	-4.806	-4.914	-5.139	-5.212	-5.359	-5.533

Solutes	Temperature (K)										
	383.15	393.15	403.15	413.15	423.15	433.15	438.15	443.15	448.15	453.15	458.15
α -Pinene	0.519	0.554	0.530	0.501	0.535	0.539	---	---	---	---	---
β -Pinene	0.208	0.196	0.141	0.162	0.097	0.162	---	---	---	---	---
α -Pinene Oxide	-0.585	-0.368	-0.336	-0.129	0.032	0.188	---	---	---	---	---
Eucalyptol	0.065	0.099	0.052	0.061	0.077	0.056	---	---	---	---	---
(-)-Menthone	-0.508	-0.544	-0.554	-0.507	-0.447	-0.441	---	---	---	---	---
p-Cymene	1.253	1.272	1.322	1.367	1.454	1.503	---	---	---	---	---
(R)-(+)-Limonene	0.357	0.365	0.393	0.442	0.486	0.553	---	---	---	---	---
Linalool	---	-0.488	0.771	2.025	3.269	4.526	---	5.864	---	---	---
(R)-(-)-Fenchone	-0.719	-0.756	-0.834	-0.828	-0.937	-0.916	---	---	---	---	---
(S)-(+)-Carvone	---	---	---	---	---	-0.706	-0.613	-0.605	-0.607	-0.691	-0.552
Geraniol	---	---	---	---	---	-7.845	-7.648	-7.554	-7.455	-7.381	-7.289
Citronellol	---	---	---	---	---	-8.510	-8.365	-8.227	-8.129	-8.067	-7.990
(-)-Isopulegol	---	---	---	---	---	-6.260	-6.177	-6.097	-5.997	-6.040	-5.877
(R)-(+)-Camphor	---	---	---	---	---	-0.704	-0.731	-0.750	-0.802	-0.664	-0.810
(L)-(-)-Menthol	---	---	---	---	---	-7.444	-7.305	-7.171	-7.097	-7.051	-6.899
(-)-Borneol	---	---	---	---	---	-11.930	-12.075	-12.282	-12.462	-12.628	-12.813

Table C.5 – Partial Excess Enthalpy at Infinite Dilution ($\bar{H}_m^{E,\infty}$) in both ILs.

Solute	Cyphos® IL 104	Cyphos® IL 101
Octane	-0.280	1.401
Nonane	-0.003	1.591
Decane	0.117	2.121
Cyclohexane	0.198	2.818
Methylcyclohexane	-0.488	1.528
Benzene	0.956	-0.571
Toluene	0.384	-0.449
Ethyl Benzene	0.588	-0.175
p-Xylene	0.308	-0.327
Thiophene	0.087	-1.915
THF	0.491	1.330
1,4-Dioxane	2.902	1.702
Diethyl Ether	-0.730	4.085
Acetone	3.362	2.078
Butanone	2.181	0.371
Methyl Acetate	2.641	2.898
Ethyl Acetate	2.120	2.505
Vinyl Acetate	2.540	2.317
Pyridine	2.344	-0.377
Acetonitrile	3.135	0.365
Methanol	-12.641	-10.402
Ethanol	-11.822	-10.307
1-Propanol	-14.376	-11.878
2-Propanol	-10.663	-11.462
1-Butanol	-14.957	-12.291
2-Butanol	-14.436	-13.360
Isobutanol	-14.504	-12.802
Tert-Butanol	-12.602	-13.583
Water	3.146	0.431
α -Pinene	0.433	0.525
β -Pinene	0.418	0.775
α -Pinene Oxide	-4.194	-6.327
Eucalyptol	0.421	0.188
(-)-Menthone	0.689	-1.247
p-Cymene	0.666	-0.763
(R)-(+)-Limonene	-1.036	-1.166
Linalool	---	-50.192
(R)-(-)-Fenchone	---	0.950
(S)-(+)-Carvone	3.841	-1.998
Geraniol	---	-16.947
Citronellol	---	-17.411
(-)-Isopulegol	---	-12.247
(R)-(+)-Camphor	---	0.233
(L)-(-)-Menthol	---	-16.249
(-)-Borneol	---	3.560

Table C.6 – Partial Excess Entropy at Infinite Dilution ($TS_m^{E,\infty}$) in Cyphos® IL 104.

Solute	Temperature (K)					
	333.15	343.15	353.15	363.15	373.15	383.15
Octane	0.166	0.182	0.180	0.202	0.162	0.209
Nonane	0.247	0.242	0.246	0.246	0.245	0.299
Decane	0.126	0.126	0.129	0.124	0.114	0.162
Cyclohexane	1.897	1.934	2.023	2.080	2.099	2.184
Methylcyclohexane	0.942	1.034	1.084	1.016	1.042	1.154
Benzene	3.026	3.083	3.167	3.263	3.364	3.474
Toluene	2.163	2.226	2.269	2.360	2.379	2.510
Ethyl Benzene	2.034	2.087	2.105	2.195	2.238	2.355
p-Xylene	1.744	1.782	1.773	1.870	1.908	2.018
Thiophene	2.482	2.549	2.624	2.726	2.751	2.862
THF	2.779	2.836	2.927	3.027	3.069	3.204
1,4-Dioxane	3.485	3.584	3.686	3.792	3.870	4.027
Diethyl Ether	0.374	0.412	0.442	0.426	0.425	0.449
Acetone	3.656	3.766	3.889	4.000	4.082	4.213
Butanone	2.971	3.048	3.131	3.230	3.289	3.433
Methyl Acetate	2.948	3.057	3.156	3.248	3.314	3.394
Ethyl Acetate	2.597	2.683	2.765	2.839	2.889	3.006
Vinyl Acetate	2.772	2.860	2.966	3.055	3.110	3.184
Pyridine	3.810	3.919	4.029	4.120	4.241	4.402
Acetonitrile	3.011	3.084	3.179	3.277	3.346	3.468

Solute	Temperature (K)					
	363.15	373.15	383.15	393.15	403.15	413.15
Methanol	-1.204	-1.200	-1.200	-1.403	-1.264	---
Ethanol	-1.569	-1.587	-1.588	-1.786	-1.682	---
1-Propanol	-3.770	-3.799	-3.884	-4.107	-4.133	---
2-Propanol	-1.550	-1.598	-1.586	-1.880	-1.616	---
1-Butanol	-4.176	-4.236	-4.272	-4.555	-4.592	---
2-Butanol	-5.176	-5.260	-5.287	-5.547	-5.750	---
Isobutanol	-3.470	-3.577	-3.337	-3.664	-3.917	---
Tert-Butanol	-4.972	-5.109	-4.884	-5.127	-5.667	---
Water	9.058	9.219	9.785	9.712	10.053	---
α -Pinene	1.540	1.562	1.633	1.680	1.692	---
β -Pinene	1.674	1.718	1.792	1.885	1.861	1.888
α -Pinene Oxide	-2.387	-2.432	---	---	-2.644	---
Eucalyptol	1.628	1.651	---	---	1.741	1.881
(-)-Menthone	1.885	1.936	---	---	2.122	2.125
p-Cymene	0.392	0.371	---	---	0.426	---
(R)-(+)-Limonene	0.063	0.070	---	---	0.072	---
Linalool	---	---	---	---	---	---
(R)-(-)-Fenchone	---	---	---	---	---	---
(S)-(+)-Carvone	---	---	---	---	4.778	4.897

Table C.7 – Partial Excess Entropy at Infinite Dilution ($TS_m^{E,\infty}$) in Cyphos® IL 101.

Solute	Temperature (K)									
	333.15	343.15	353.15	363.15	373.15	383.15	393.15	403.15	413.15	
Octane	-0.157	-0.168	-0.153	-0.147	-0.168	-0.192	---	---	---	
Nonane	-0.173	-0.175	-0.176	-0.138	-0.181	-0.217	---	---	---	
Decane	0.069	0.098	0.066	0.097	0.079	0.090	---	---	---	
Cyclohexane	2.588	2.684	2.725	2.889	2.844	3.004	---	---	---	
Methylcyclohexane	1.155	1.217	1.234	1.310	1.301	1.332	---	---	---	
Benzene	1.382	1.446	1.484	1.522	1.575	1.586	---	---	---	
Toluene	0.997	1.031	1.058	1.056	1.111	1.161	---	---	---	
Ethyl Benzene	0.794	0.825	0.881	0.870	0.907	0.913	---	---	---	
p-Xylene	0.556	0.566	0.589	0.582	0.635	0.633	---	---	---	
Thiophene	0.948	0.983	1.015	1.023	1.081	1.086	---	---	---	
THF	2.627	2.707	2.780	2.882	2.994	2.983	---	---	---	
1,4-Dioxane	2.342	2.403	2.472	2.544	2.651	2.669	---	---	---	
Diethyl Ether	3.394	3.439	3.465	3.676	3.858	3.808	---	---	---	
Acetone	2.712	2.810	2.852	2.970	3.100	3.083	---	---	---	
Butanone	1.241	1.307	1.331	1.380	1.389	1.443	---	---	---	
Methyl Acetate	2.658	2.923	2.836	2.975	3.094	3.093	---	---	---	
Ethyl Acetate	2.222	2.310	2.362	2.448	2.545	2.528	---	---	---	
Vinyl Acetate	2.326	2.424	2.473	2.558	2.656	2.657	---	---	---	
Pyridine	2.019	2.104	2.167	2.190	2.305	2.318	---	---	---	
Acetonitrile	1.959	2.038	2.091	2.148	2.217	2.251	---	---	---	
Methanol	---	---	---	-0.087	-0.054	-0.075	-0.064	-0.070	-0.096	
Ethanol	---	---	---	-0.776	-0.761	-0.773	-0.790	-0.811	-0.894	
1-Propanol	---	---	---	-2.009	-2.000	-2.097	-2.147	-2.195	-2.268	
2-Propanol	---	---	---	-2.530	-2.540	-2.599	-2.679	-2.759	-2.871	
1-Butanol	---	---	---	-2.318	-2.305	-2.369	-2.448	-2.517	-2.622	
2-Butanol	---	---	---	-4.247	-4.305	-4.412	-4.541	-4.670	-4.821	
Isobutanol	---	---	---	-2.491	-2.506	-2.591	-2.655	-2.719	-2.831	
Tert-Butanol	---	---	---	-5.354	-5.485	-5.589	-5.766	-5.927	-6.087	
Water	---	---	---	5.237	5.345	5.570	5.644	5.790	5.964	

Solute	Temperature (K)										
	383.15	393.15	403.15	413.15	423.15	433.15	438.15	443.15	448.15	453.15	458.15
α -Pinene	0.005	-0.030	-0.005	0.024	-0.011	-0.014	---	---	---	---	---
β -Pinene	0.567	0.580	0.634	0.613	0.678	0.613	---	---	---	---	---
α -Pinene Oxide	-5.742	-5.959	-5.991	-6.197	-6.358	-6.514	---	---	---	---	---
Eucalyptol	0.123	0.089	0.137	0.128	0.111	0.133	---	---	---	---	---
(-)-Menthone	-0.739	-0.702	-0.693	-0.740	-0.800	-0.806	---	---	---	---	---
p-Cymene	-2.017	-2.036	-2.085	-2.131	-2.218	-2.267	---	---	---	---	---
(R)-(+)-Limonene	-1.523	-1.531	-1.559	-1.608	-1.652	-1.720	---	---	---	---	---
Linalool	---	-49.704	-50.963	-52.217	-53.460	-54.717	---	-56.055	---	---	---
(R)-(-)-Fenchone	1.669	1.705	1.784	1.777	1.886	1.865	---	---	---	---	---
(S)-(+)-Carvone	---	---	---	---	---	-1.292	-1.385	-1.393	-1.390	-1.307	-1.446
Geraniol	---	---	---	---	---	-9.102	-9.299	-9.393	-9.492	-9.566	-9.658
Citronellol	---	---	---	---	---	-8.900	-9.045	-9.183	-9.282	-9.343	-9.420
(-)-Isopulegol	---	---	---	---	---	-5.988	-6.070	-6.151	-6.250	-6.207	-6.370
(R)-(+)-Camphor	---	---	---	---	---	0.937	0.964	0.984	1.035	0.897	1.044
(L)-(-)-Menthol	---	---	---	---	---	-8.804	-8.944	-9.078	-9.152	-9.197	-9.350
(-)-Borneol	---	---	---	---	---	15.490	15.635	15.842	16.022	16.188	16.373

Table C.8 - Gas-liquid partition coefficient in Cyphos® IL 104.

Solute	Temperature (K)					
	333.15	343.15	353.15	363.15	373.15	383.15
Octane	353.905	240.426	166.964	120.001	86.519	65.581
Nonane	861.624	554.240	369.329	253.030	177.920	130.423
Decane	2073.545	1276.415	814.666	535.238	361.664	255.554
Cyclohexane	113.969	83.548	63.751	49.070	38.001	30.563
Methylcyclohexane	195.234	142.702	105.221	76.293	58.287	46.597
Benzene	129.028	94.158	70.977	54.809	43.199	34.712
Toluene	324.738	228.168	163.321	121.587	90.221	70.728
Ethyl Benzene	714.334	481.173	329.356	237.132	171.964	130.453
p-Xylene	770.851	515.289	348.827	251.141	181.511	137.075
Thiophene	166.742	120.592	89.586	68.624	52.284	41.707
THF	88.003	65.088	49.804	38.972	30.466	24.945
1,4-Dioxane	162.150	117.268	86.817	65.696	50.205	40.050
Diethyl Ether	21.733	17.032	13.564	10.822	8.822	7.352
Acetone	31.744	24.657	19.605	15.791	12.804	10.699
Butanone	81.539	60.277	45.674	35.502	27.753	22.676
Methyl Acetate	32.592	25.125	19.702	15.720	12.659	10.413
Ethyl Acetate	68.929	50.863	38.402	29.545	23.013	18.652
Vinyl Acetate	53.948	40.253	30.908	24.082	18.909	15.209
Pyridine	360.985	252.812	181.743	132.896	100.253	78.058
Acetonitrile	64.059	48.174	37.217	29.308	23.225	19.007

Solute	Temperature (K)					
	363.15	373.15	383.15	393.15	403.15	413.15
Methanol	609.282	411.219	284.108	188.768	142.282	---
Ethanol	658.534	432.589	293.545	192.375	141.553	---
1-Propanol	1522.77	965.394	620.675	394.105	273.354	---
2-Propanol	519.387	338.728	232.193	149.023	150.81	---
1-Butanol	3533.39	2133.96	1345.22	811.363	544.493	---
2-Butanol	1058.33	667.244	443.004	282.382	188.949	---
Isobutanol	2606.17	1566.34	1089.26	655.161	416.968	---
Tert-Butanol	324.193	210.3	158.017	105.497	66.4083	---
Water	339.592	240.365	197.4	135.142	106.965	---
α -Pinene	361.51	255.506	187.527	139.267	104.284	---
β -Pinene	518.979	364.768	264.663	197.076	144.277	109.235
α -Pinene Oxide	1475.36	992.286	---	---	351.869	---
Eucalyptol	741.195	507.483	---	---	187.8	144.802
(-)-Menthone	2569.54	1671.14	---	---	552.741	394.451
p-Cymene	741.459	504.562	---	---	190.394	---
(R)-(+)-Limonene	739.983	506.367	---	---	186.412	---
Linalool	---	---	---	---	2548.34	---
(R)-(-)-Fenchone	---	---	---	---	348.083	---
(S)-(+)-Carvone	---	---	---	---	1004.08	716.651

Table C.9 - Gas-liquid partition coefficient in Cyphos® IL 101.

Solute	Temperature (K)									
	333.15	343.15	353.15	363.15	373.15	383.15	393.15	403.15	413.15	
Octane	255.775	175.803	125.305	91.283	67.447	50.840	---	---	---	
Nonane	620.307	408.013	276.949	195.789	138.303	100.264	---	---	---	
Decane	1467.366	932.741	600.184	407.103	279.288	198.492	---	---	---	
Cyclohexane	84.601	64.617	49.425	40.133	30.946	25.891	---	---	---	
Methylcyclohexane	151.655	111.778	83.037	64.266	49.285	38.993	---	---	---	
Benzene	184.171	134.913	100.239	76.067	59.151	46.185	---	---	---	
Toluene	428.892	299.451	213.981	155.025	116.877	89.682	---	---	---	
Ethyl Benzene	895.624	601.784	419.443	293.321	213.379	157.103	---	---	---	
p-Xylene	940.314	626.309	431.113	301.485	220.217	161.439	---	---	---	
Thiophene	294.094	209.295	152.599	112.934	86.733	66.756	---	---	---	
THF	91.656	69.075	53.042	41.933	33.825	26.664	---	---	---	
1,4-Dioxane	246.448	175.824	128.678	96.335	74.368	56.804	---	---	---	
Diethyl Ether	16.931	13.559	10.978	9.606	8.421	6.940	---	---	---	
Acetone	53.459	41.198	31.773	25.597	21.033	16.737	---	---	---	
Butanone	125.020	91.994	68.273	52.209	40.189	31.955	---	---	---	
Methyl Acetate	39.853	32.633	24.124	19.656	16.179	13.026	---	---	---	
Ethyl Acetate	78.014	58.110	43.743	34.056	27.116	21.207	---	---	---	
Vinyl Acetate	74.163	55.658	42.000	32.771	26.164	20.609	---	---	---	
Pyridine	752.268	517.353	362.782	257.301	192.437	142.139	---	---	---	
Acetonitrile	177.345	131.306	98.350	75.188	58.750	46.131	---	---	---	
Methanol	---	---	---	625.990	430.887	298.479	213.651	155.319	114.444	
Ethanol	---	---	---	772.511	516.283	351.241	244.664	174.176	124.466	
1-Propanol	---	---	---	1777.415	1148.422	740.178	498.440	344.945	242.888	
2-Propanol	---	---	---	728.858	481.934	323.557	222.129	156.642	112.271	
1-Butanol	---	---	---	4029.385	2509.596	1577.907	1019.731	680.665	461.798	
2-Butanol	---	---	---	1502.101	956.014	619.899	411.998	282.044	197.003	
Isobutanol	---	---	---	3056.291	1905.137	1202.985	790.284	534.953	367.147	
Tert-Butanol	---	---	---	588.883	380.768	256.844	174.610	122.771	88.611	
Water	---	---	---	350.869	246.547	183.738	133.149	100.493	77.742	

Solute	Temperature (K)										
	383.15	393.15	403.15	413.15	423.15	433.15	438.15	443.15	448.15	453.15	458.15
α -Pinene	162.916	119.681	91.192	70.763	54.758	43.393	---	---	---	---	---
β -Pinene	240.079	176.665	134.105	101.287	79.696	61.351	---	---	---	---	---
α -Pinene Oxide	719.596	491.900	365.159	263.311	196.617	149.890	---	---	---	---	---
Eucalyptol	350.664	249.712	185.989	138.721	105.061	81.727	---	---	---	---	---
(-)-Menthone	1304.027	901.529	633.999	448.814	323.623	241.770	---	---	---	---	---
p-Cymene	391.462	282.116	205.771	153.221	114.821	88.466	---	---	---	---	---
(R)-(+)-Limonene	334.187	241.918	177.760	132.411	100.624	77.266	---	---	---	---	---
Linalool	---	7143.735	4199.120	2552.921	1603.423	1029.975	---	663.212	---	---	---
(R)-(-)-Fenchone	751.784	528.143	383.692	277.115	210.775	157.067	---	---	---	---	---
(S)-(+)-Carvone	---	---	---	---	---	488.150	405.768	346.847	298.478	263.458	220.128
Geraniol	---	---	---	---	---	4607.232	3577.277	2873.438	2317.520	1891.324	1543.834
Citronellol	---	---	---	---	---	4476.768	3511.699	2778.191	2235.604	1827.219	1495.602
(-)-Isopulegol	---	---	---	---	---	1067.252	875.241	722.146	595.830	513.324	420.668
(R)-(+)-Camphor	---	---	---	---	---	240.866	211.322	185.752	165.307	140.390	129.056
(L)-(-)-Menthol	---	---	---	---	---	2272.825	1810.619	1452.930	1191.510	989.409	802.609
(-)-Borneol	---	---	---	---	---	3484.674	2771.860	2256.201	1834.050	1494.453	1231.398