PEGs in the Fractionation of Terpenes from Lemon Essential Oil

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Abstract

The main objective of this work is to study the potential use of polyethylene glycol 400 (PEG400) as a mass separation agent in the fractionation of terpenes that compose several essential oils, including citrus oils. Both terpenes and their oxygenated derivatives (terpenoids) are common ingredients in fragrances, pharmaceuticals, food additives, polymers, biofuels and fine-chemical products. Though limited information exists on the application of PEGs for this purpose, these polymers are also already used in the cosmetics and pharmaceutical areas.

To achieve this, the infinite dilution activity coefficients of 39 solutes (water, alkanes, cycloalkanes, ketones, ethers, cyclic ethers, esters, alcohols, and 16 terpenes and terpenoids) were measured in PEG400 by inverse gas chromatography in the interval of 60 °C to 120 °C. This technique is very useful and cost-effective to do a preliminary solvent screening, allowing the calculation of several separation parameters such as selectivities, capacities and solvent performance indices (Q_{ij}), which are key values to design a separation process. In general, alkanes, cycloalkanes, hydrocarbon terpenes and terpenoids presented the highest activity coefficients, with positive deviations to ideality. On the other hand, water and most alcohols with less than 4 carbon atoms presented activity coefficients lower than 1.

Among the binary mixtures of terpenes studied (limonene + carvone, limonene + linalool, menthone + menthol, borneol + camphor, α-pinene + β-pinene, α-pinene + limonene, and *p*-cymene + limonene), satisfactory results were obtained only for the mixtures limonene + linalool and limonene + carvone, with Q_{ij} of 1.5 and 2.4, respectively. For the remaining ones, the low capacities of the solutes resulted in Q_{ij} lower than 1. As expected, the separation of mixtures containing two hydrocarbon terpenes is the most difficult. Nevertheless, for the mixtures α-pinene/β-pinene and *p*-cymene/limonene, satisfactory selectivities of 1.3 were obtained. Future studies with PEGs of different molecular weights or end chains may allow to modulate the polarity and improve the solubility of both terpenes and terpenoids in the solvent.

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

Resumo

O principal objetivo deste trabalho é estudar a potencial utilização do polietilenoglicol 400 (PEG400) como agente de separação de massa no fracionamento de terpenos que compõem diversos óleos essenciais, incluindo óleos cítricos. Tanto os terpenos como os seus derivados oxigenados (terpenóides) são ingredientes comuns em fragrâncias, produtos farmacêuticos, aditivos alimentares, polímeros, biocombustíveis e produtos de química fina. Embora existam poucos estudos sobre a aplicação de PEG para este fim, estes polímeros também já são utilizados nas áreas cosmética e farmacêutica.

Para este fim, os coeficientes de atividade a diluição infinita de 39 solutos (água, alcanos, cicloalcanos, cetonas, éteres, éteres cíclicos, ésteres, álcoois e 16 terpenos e terpenóides) foram medidos em PEG400 por cromatografia gasosa inversa no intervalo de 60 °C a 120 °C. Esta técnica é muito útil e eficiente para levar a cabo uma seleção preliminar de solventes, permitindo o cálculo de vários parâmetros de separação, tais como seletividades, capacidades e índices de desempenho de solventes (Q_{ij}), que são valores-chave para projetar um processo de separação. Em geral, alcanos, cicloalcanos, terpenos de hidrocarbonetos e terpenoides apresentaram os maiores coeficientes de atividade, com desvios positivos à idealidade. Por outro lado, a água e a maioria dos álcoois com menos de 4 átomos de carbono apresentaram coeficientes de atividade inferiores a 1.

Entre as misturas binárias de terpenos estudadas (limoneno + carvona, limoneno + linalol, mentona + mentol, borneol + cânfora, α-pineno + β-pineno, α-pineno + limoneno e *p*-cimene + limoneno), foram obtidos resultados satisfatórios para as misturas limoneno/linalol e limoneno/carvona, com Q_{ij} de 1,5 e 2,4, respectivamente. Para os restantes, as baixas capacidades dos solutos resultaram em Q_{ij} inferiores a 1. Como esperado, a separação de misturas contendo dois terpenos de hidrocarbonetos é a mais desafiante. No entanto, para as misturas α-pineno + β-pineno e *p*-cimeno + limoneno, obtiveram-se valores de seletividade satisfatórios (1,3). Estudos futuros com PEGs de diferentes pesos moleculares ou cadeias terminais poderão permitir modular a polaridade e melhorar a solubilidade de terpenos e terpenoides no solvente.

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

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List of Symbols

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B_{ab}	Crossed Second Virial Coefficient [m^3/mol]
B_{aa}	Second Virial Coefficient of Pure Compound a [m^3/mol]
$G_m^{E,\infty}$	Excess Gibbs Free Energy at Infinite Dilution [kJ/mol]
$H_m^{E,\infty}$	Excess Enthalpy at Infinite Dilution [kJ/mol]
J_2^3	Pressure Correction Term
K_j^∞	Capacity of the Solute j
n_a	Number of Moles of Compound a [mol]
P_a^*	Vapor Pressure of Pure Compound a [Pa]
P_i	Column Inlet Pressure [Pa]
P_f	Column Outlet Pressure [Pa]
R	Pressure Measured by the Flowmeter [Pa]
$T_{ref}S_m^{E,\infty}$	Ideal Gas Constant [kJ/(mol·K)]
S_{ij}^∞	Excess Entropy at Infinite Dilution [kJ.K/mol]
t_a	Selectivity between the Solutes i and j
T	Retention Time of Compound a [s]
T_f	Temperature Inside the Oven of the Gas-Chromatograph [K]
U	Volumetric Flow Measured by the Flowmeter [m /s]
U_0	Column Outlet Volumetric Flow Rate [m /s]
V_a	Molar Volume of Pure Compound a [m^3/mol]
V_N	Net Retention Volume [m^3]
V_a^∞	Partial Molar Volume of Pure Compound a at Infinite Dilution [m3/mol]

Greek letters

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

Abbreviations

PEG	Poly (ethylene glycol)

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Chapter 1. Scope and objectives

Terpenes represent a wide variety of compounds with multiple applications in the food, cosmetic and pharmaceutical industries. They are the main components of essential oils, which are usually composed of a mixture of oxygenated (terpenoids) and hydrocarbon terpenes. The removal of the hydrocarbon terpenes fraction from the essential oils, called deterpenation, is desired in many cases, as it contributes to the stability of the oil, increasing its associated value. Within the available methods to perform this process, liquid-liquid extraction or vacuum distillation have been proposed, often combined with the use of mass separation agents (MSAs) such as water, organic solvents, eutectic solvents or ionic liquids (ILs). Besides the separation of terpenoids from hydrocarbon terpenes, another separation worthy of attention is α-pinene/β-pinene, since the pure pinenes can be used as precursors in the synthesis of many other terpenes such as linalool, geraniol or camphor, adding value to materials of forest origin such as the turpentine oil.

This work offers a new approach for the fractionation and purification of terpenes using polyethylene glycols (PEGs) as MSAs. In particular, the fractionation of lemon essential oils rich in terpenes such as α-pinene, β-pinene, limonene, myrcene, eucalyptol, linalool, or borneol will be studied in more detail. The selection of these compounds reflects their industrial importance and their significant presence in several essential oils, namely the lemon essential oil as well as their organic functional variety.

Overall, the main objectives of this work are:

- Measurement by inverse gas chromatography of the infinite dilution activity coefficients of water, common organic solutes (alkanes, cycloalkanes, ketones, ethers, cyclic ethers, aromatic hydrocarbons, esters, alcohols), terpenes and terpenoids in PEGs of different molecular weights.
- Evaluation of the thermodynamic parameters (excess partial molar properties, selectivities, capacities, gas-liquid partition coefficients, and solvent performance indexes) of the solutes in the PEGs, to and infer the performance of the polymers as MSAs in different separation processes (monoterpene/monoterpene and monoterpene/monoterpenoid).

Chapter 2. Introduction

2.1 The role of polyethylene glycol as solvent

Polyethylene glycol (PEG) is a non-volatile poly-ether compound with many applications, being considered a green alternative solvent.[1] PEGs of different molecular weights are employed as excipients in pharmaceutical preparations and cosmetic products due to their extremely low toxicities.[2] It is also a widely recognized phase transfer catalyst[3,4], and can be used as a stationary phase in gas chromatography,[5,6] as well as an affordable, safe, and ecologically friendly solvent for reaction media.[7] Polyethylene glycol is also used to dissolve a wide range of materials such as mineral salts.[7] Either pure or in aqueous solutions, it can replace more costly and/or hazardous solvents, like supercritical carbon dioxide, ionic liquids, and micellar systems in reactions like oxidation, reduction, and substitution.[1] Another utilization proposed in the literature results from the combination of PEGs with other ingredients. In a process known as PEGylation, ILs and other compounds have been chemically attached to PEGs.[7]

PEGs have also been used as solvents in the extraction of biomolecules from natural products. For example, an aqueous solution of polyethylene glycol 400 (PEG400) coupled with an ultrasonic–microwave-assisted technique was used to extract polysaccharides from *Pericarpium granati* and, after, to precipitate them from the extraction solution.[8] Better results were obtained when compared to the use of pure water. In another study, the chemical composition and biological activities of two propolis extracts were compared: one obtained with PEG 400 and another with ethanol.[9] Though PEG400 resulted in a lower yield of propolis extract than ethanol, similar total phenolic content and antioxidant activity were obtained.

Polyethylene glycol (PEG200), with an average molecular weight of 200 g/mol, also found application as a solvent and phase-transfer catalyst in organic synthesis,[6] as well as a green reaction medium in various organic reactions, including those conducted in water and aqueous solutions. It is also used in biotechnology and medicine, namely as tissue culture media and organ preservation.[6] Additionally, PEG200 findsapplication in green catalytic oxidation systems and alternative wood pulping processes due to its metal ion coordination properties. [6] Physically, PEG200 appears as a colourless viscous liquid at room temperature and is FDA-approved for internal consumption.[6]

In the pharmaceutical area, polyethylene glycol 600 (PEG600) serves as a solvent and solubilizing agent for active substances and excipients.[10] It can be paired with surfactants to enhance the solubilization of poorly water-soluble active pharmaceutical ingredients (APIs).[10] Cosmetically, PEG600 acts as a moisturizer in tooth pastes, facial cleaning foams, hair-care products, and wet tissues. Industrially, it functions as a lubricant in textile processing, a cutting oil, a solvent cleaner, and an emulsifier for herbicides and fungicides.[10] Its green properties and biodegradability further enhance its interest and applications. Overall, the mentioned PEGs, with their versatility and safety, play crucial roles in various fields, from pharmaceuticals to cosmetics.[10]

In this work, the aim is to evaluate the use of low molecular PEGs as MSA to separate different terpenes mixtures. To design such processes, it is necessary to collect industrially relevant physical properties of these polymers as a function of their molar mass, such as density, viscosity, vapor pressure, melting temperature, among others. Recently, Hoffmann (2022)[7] reported a summary of those properties that are included in **Table 1**, for PEG 200, 400 and 600.

Table 1. Thermophysical properties of PEGs with different average molar mass.

PEG average molar mass (g·mol^{-1})	**200**	**400**	**600**
	T = 298.15 K, ambient pressure		
Density/g·cm^{-3}	1.12036[11]	1.12239[16]	1.1214[17]
Viscosity/mPa·s	49.45[12]	92.797[18]	135.73[17]
Dielectric constant	19.69[13]	11[19]	10.71[19]
Melting temperature (K)	218-233[20]	290 to 295[20]	290 to 295[20]
	T = 368.2 K		
Vapor pressure (Pa)	9.9[20]	-	0.2[20]

As can be seen in Table 1, in the molecular weight range of the selected PEGs, the density does not significantly change, but there is an expected increase of the viscosity with the molecular weight and a decrease of the dielectric constant. The vapor pressure available in the literature, only at 368 K, shows that these solvents have very low volatility which reduces their environmental ubiquity. The melting temperature ranges indicate that these PEGS can be applied as solvents at moderate temperatures.

2.2 Thermodynamic background

2.2.1 Infinite dilution activity coefficients

The infinite dilution activity coefficients (γ_{13}^{∞}) of a solute (1) partitioning between a carrier gas (2) and stationary non-volatile liquid phase (3) can be calculated using the following equation, developed by Everett and Cruickshank:[14,15]

$$ln(\gamma_{13}^{\infty}) = ln\left(\frac{n_3 RT}{V_N P_1^*}\right) - \frac{P_1^*(B_{11} - V_1^*)}{RT} + \frac{P_0 J_2^3 (2B_{12} - V_1^{\infty})}{RT} \quad (1)$$

where n_3 is the mole number of solvent on the column packing, R is the ideal gas constant, P_1^* is the saturated vapor pressure of the solute, P_0 is the column outlet pressure, B_{11} is the second virial coefficient of the pure solute, V_1^* is the molar volume of the solute, B_{12} is the crossed second virial coefficient of the solute and the carrier gas (helium), $V_1^{\infty}$is the partial molar volume of the solute at infinite dilution in the solvent, V_N is the net retention volume of the solute, T is the absolute temperature of the column (regulated by the GC oven). In Eq (1), J_2^3 is the pressure correction term, as discussed in detail by Everett,[15] and is given by Eq. (2):

$$J_2^3 = \frac{2\left({}^{P_i}/_{P_0}\right)^3 - 1}{3\left({}^{P_i}/_{P_0}\right)^2 - 1} \quad (2)$$

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

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

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

$$U_0 = U \frac{P_f}{P_0} \frac{T}{T_f} \quad (4)$$

where U_0, P_f and T_f are the volumetric flow, the pressure, and the temperature measured by the flowmeter after the carrier gas goes through the detector, respectively. The second order virial

coefficients, used in Eq (1), were estimated using the correlation proposed by Tsonopoulos and discussed in detail by Poling.[14]

2.2.2 *Infinite dilution excess partial molar properties*

The infinite dilution excess partial molar properties, namely the excess partial molar Gibbs energy $\bar{G}_m^{E,\infty}$, enthalpy ($\bar{H}_m^{E,\infty}$) and entropy ($\bar{S}_m^{E,\infty}$) of the solute, can be determined using the Gibbs-Helmholtz Equation. These thermodynamic properties and the measured γ_{13}^{∞} data support an interpretation of the molecular interactions in the mixture. From the linear dependence of γ_{13}^{∞} with temperature (van't Hoff plot), both $\bar{H}_m^{E,\infty}$ and $\bar{S}_m^{E,\infty}$ can be calculated, using the following equations:

$$\ln \gamma_{13}^{\infty} = \frac{\bar{H}_m^{E,\infty}}{R}\frac{1}{T} - \frac{\bar{S}_m^{E,\infty}}{R} \tag{5}$$

$$\bar{G}_m^{E,\infty} = RTln\gamma_{13}^{\infty} \tag{6}$$

$$\bar{G}_m^{E,\infty} = \bar{H}_m^{E,\infty} - \bar{S}_m^{E,\infty}T_{ref} \tag{7}$$

at a reference temperature T_{ref}.

2.2.3 *Separation factors*

To assess the efficacy of PEG as an entrainer in several chemical separation problems, it is possible to calculate the selectivity (S_{ij}^{∞}) between the solutes *i* and *j* and the separation capacity (k_j^{∞}), as follows:

$$S_{ij}^{\infty} = \frac{\gamma_{i3}^{\infty}}{\gamma_{j3}^{\infty}} \tag{8}$$

$$k_j^{\infty} = \frac{1}{\gamma_{j3}^{\infty}} \tag{9}$$

where *j* is the solute with the lowest infinite dilution activity coefficient for a given separation of two components, and 3 indicates the solvent. High selectivities and capacities are desirable for a good separation agent. The solvent performance index, also defined at infinite dilution, combines both contributions as it can be calculated using Eq (10):

$$Q_{ij}^{\infty} = S_{ij}^{\infty}k_j^{\infty} \tag{10}$$

Chapter 3. State of the art

The deterpenation and other separation problems involving terpene mixtures have been addressed before using different classes of mass separation agents. In this section, a review is presented on the use of low volatile MSA such as ionic liquids and PEGs. For the latter, there is limited information on their application in separation processes involving terpenes mixtures, so information about other solutes was also collected.

3.1 Ionic liquids

In previous works, several ionic liquids have been studied as mass separation agents of different essential oils as reviewed by Zambom et al.[16]. In **Table 2**, a summary of the separation factors for important binary mixtures containing limonene, linalool, and pinenes isomers is presented. Those values were calculated using infinite dilution activity coefficients of terpenes in ionic liquids measured by inverse gas chromatography.[16]

Table 2. Selectivities, S_{ij}^{∞}, capacities, k_j^{∞}, and solvent performance indexes, Q_{ij}^{∞}, at infinite dilution for different terpenes mixtures in several ionic liquids at 403.2 K.[16]

Ionic liquid	S_{ij}^{∞} / k_j^{∞} / Q_{ij}^{∞}			Source
	α-pinene/β-pinene	β-pinene/limonene	limonene/linalool	
[C4mim][PF6]	1.49/0.03/0.04	1.04/0.04/0.42	3.02/0.11/0.33	[16]
[C4mim][PF6]/[C4mim]Cl	1.69/0.03/0.05	1.02/0.03/0.03	10.3/0.26/2.68	[16]
[P6,6,6,14]Cl	1.27/1.10/1.40	1.25/1.10/1.38	10.2/9.01/91.9[a]	[17]
[P6,6,6,14][(C8H17)2PO2]	1.07/1.58/1.69	1.15/1.58/1.82	5.93/8.2/48.6	[17]
[C4mim][OAc]	1.33/0.06/0.08	1.35/0.06/0.08	30.3/1.26/38.2	[17]
[C8mim]Cl	1.37/0.08/0.11	1.07/0.09/0.10	15.4/1.34/20.6[a]	[18]
[C4mim]Cl/[C12mim]Cl	1.44/0.11/0.16	1.04/0.11/0.11	14.1/1.54/21.7[a]	[18]
[C12mim]Cl	1.24/0.24/0.30	1.01/0.24/0.24	9.65/2.27/21.9[a]	[18]

As discussed by Zambom *et al.*[16], for [C4mim][PF6], low selectivities and very low solvent performance indexes were obtained for all the studied mixtures. The addition of [C4mim]Cl led to interestingly increased selectivities for the limonene/linalool mixture.

The set of ILs [P6,6,6,14]Cl and [P6,6,6,14] [(C8H17)2PO2] resulted in the highestselectivities for α-pinene/β-pinene and β-pinene/limonene, though moderate values were still achieved. On the

other hand, $[P_{6,6,6,14}]Cl$ was the best IL for the separation of the mixture limonene/linalool, with a $\boldsymbol{Q_{ij}^{\infty}} = 91.9$.

The remaining ILs ($[C_4mim][OAc]$, $[C_8mim]Cl$, $[C_4mim]Cl/[C_{12}mim]Cl$ and $[C_{12}mim]Cl$) were not suitable as entrainers for the separation of the mentioned monoterpene/monoterpene pairs, as indicated by the low-performance indexes ranging between 0.08 and 0.30. They were nevertheless good alternatives for the monoterpene/monoterpenoid mixture, with Q_{ij}^{∞} ranging between 20.6 and 38.2.

Overall, these results can help guide the selection of ionic liquids, in the optimization of terpene separation processes, though the separation of monoterpene/monoterpene remains challenging.[16]

3.2 Polyethylene glycol

In the literature, there are already some works reporting infinite dilution activity coefficients data of different organic solutes in PEGs of varying molecular weight, measured by inverse gas chromatography. In this section, a review of that information is provided.

Diaz et al.[19] studied the ability of several liquid phases in the separation of pine terpenes by inverse gas chromatography. The solutes include three monocyclic (limonene, α-phellandrene and *p*-cymene) and three bicyclic (α-pinene, β-pinene and campheneterpenes. The six solvents investigated were liquid organic phases of increasing polarity, with different functional groups, namely:

- Dinonyl phthalate (DNP),
- Amine 220 (A-220),
- Tricresyl phosphate (TCP),
- Carbowax 6000 (PEG6000),
- Ethylene glycol phthalate (EGP),
- Carbowax 1500 (PEG1500).

The stationary phase was composed of the support Chromosorb **P-AW** (60/80 mesh), coated with 15% (*w/w*) of liquid phase.

The authors found that, by injecting around 0.02 μL of solute at three different temperatures, the γ_{13}^{∞} values obtained are close to unity in DNP and PEG1500, while values ranging from 1.5 to 5.8 were found for A-220, TCP and EGP. For the polyethylene glycol liquid phase, two

different molecular weights were tested, 1500 and 6000. It was observed that the γ_{13}^{∞} is decreases as the molecular weight increases. γ_{13}^{∞} lower than unity was obtained for various terpenes in PEG6000, indicating better solubility in this liquid phase compared to PEG1500, where the polarity is higher. As a general trend, the lowest activity coefficients are achieved in the solvent PEG6000. Figure 1 shows the results obtained at 80 ºC.

In addition, the study of Diaz et al.[19] demonstrated that at the operating temperatures (in the range of 80 ºC to 120 ºC), the selectivities at infinite dilution of the mixtures α-pinene/β-pinene, α-pinene/camphene, α-pinene/α-phellandrene, α-pinene/limonene and *p*-cymene/α-pinene did not significantly changed. It should be highlighted that selectivities higher than 1 (S_{ij}^{∞} = 1.39-1.43) were obtained for the mixture α-pinene/β-pinene, using PEG1500 and PEG6000, which is a very promising result considering the difficulty of separating these compounds.

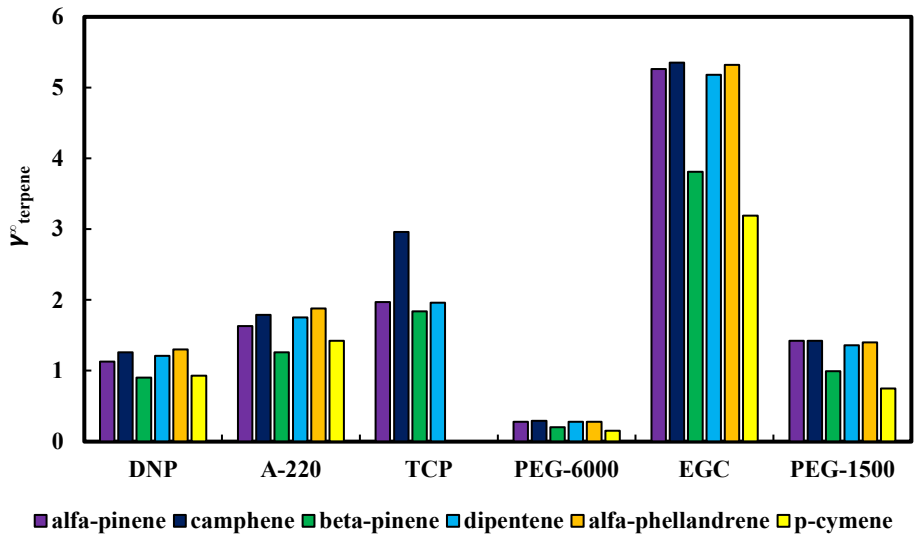


Figure 1. Infinite dilution activity coefficients of terpenes in different stationary phases at 100 ºC, as reported by Diaz et al. (2004).[19]

In another context, the correlation between the physical properties and the structure of alcohols and their gas chromatographic behaviour on polar and non-polar stationary phases have been investigated.[20] Primary and secondary straight-chain alcohols with one to eight carbon atoms have been analysed by gas chromatography at 100ºC on 3 m columns packed with 20% of squalene and PEG400, 1000 and 20000. The inert support of the stationary phase was chlorodimethylsilane-treated Chromosorb W (60-80 mesh). Hamilton micro syringes were

used to inject decreasing volumes of the alcohols into the columns in order to calculate the retention time at zero concentration using extrapolation.

Figures 2 and 3 show the infinite dilution activity coefficients of the studied solutes in PEG400 (a stationary phase that will also be used in this work) as a function of the number of carbon atoms (*n*) of alcohols (methanol, ethanol and other alcohols with the hydroxyl group in positions 1, 2 or 3 of the alkyl chain) and linear alkanes, respectively.[17]

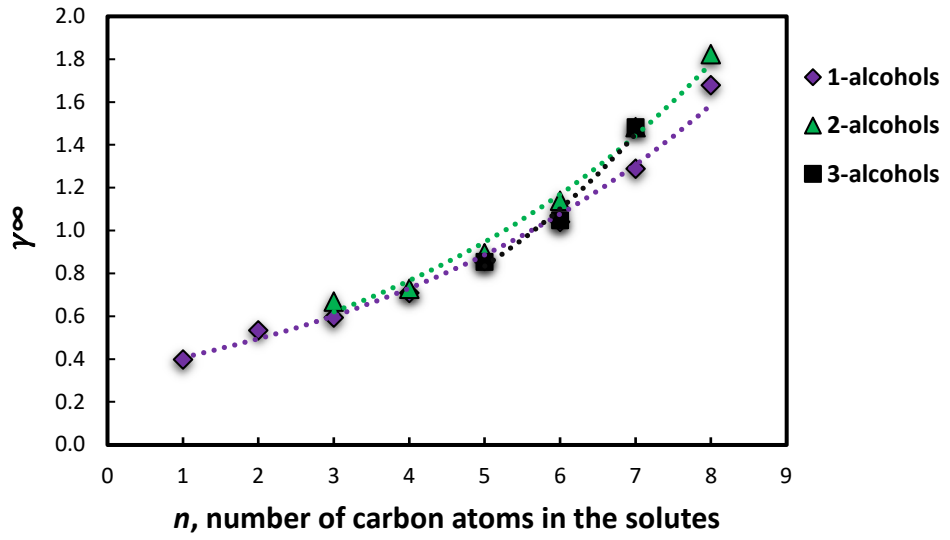


Figure 2. Infinite dilution activity coefficients of alcohols in PEG400, at 100 °C, reported by Castello and D'Amato.[20]

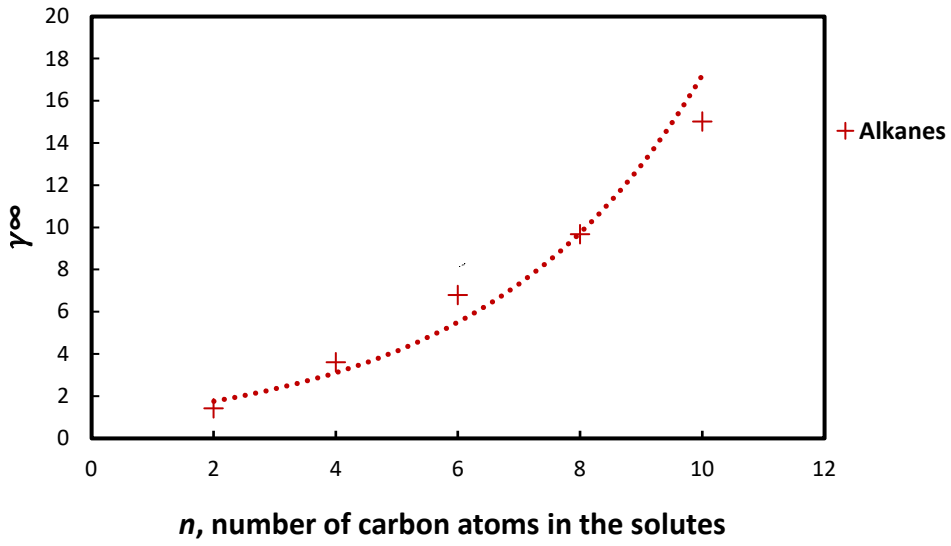


Figure 3. Infinite dilution activity coefficients of alkanes in PEG400, at 100 °C, reported by Castello and D'Amato.[20]

As can be seen by Figure 2, the location of the OH group (carbon 1, 2 or 3) does not greatly affect the values of γ_{13}^{∞} in the isomeric alcohols. In general, the γ_{13}^{∞} of alcohols and alkanes increased with *n*, being higher than 1 for all alkanes and alcohols with $n \geq 6$ (Figure 3). The lower molecular weight alcohols have higher affinity towards PEG400, showing in some cases negative deviations to the ideal solution behaviour ($\gamma < 1$).

Bestani and Shing[21] conducted a study to measure the infinite dilution activity coefficients of water ($\gamma_{\mathrm{H2O}}^{\infty}$) in triethylene glycol (TEG), polyethylene glycols with varying molecular weights (M_w = 400, 600, 1000, 1500 and 7500), glycerol and their respective mixtures.[21] The measurements were obtained using the gas-liquid partition chromatography method within the temperature range of 50 to 140°C. This study aims to contribute with valuable information about water behavior in these solvents, which has implications for various industrial processes such as natural gas dehydration and chemical engineering applications.[21] This information is also very relevant for the purification of these solvents, as they are usually very hygroscopic. The authors assessed the dehydrating efficacy of the studied solvents based on their molecular weight, by comparing the corresponding infinite dilution activity coefficients of water, as represented in Figure 4.[21]

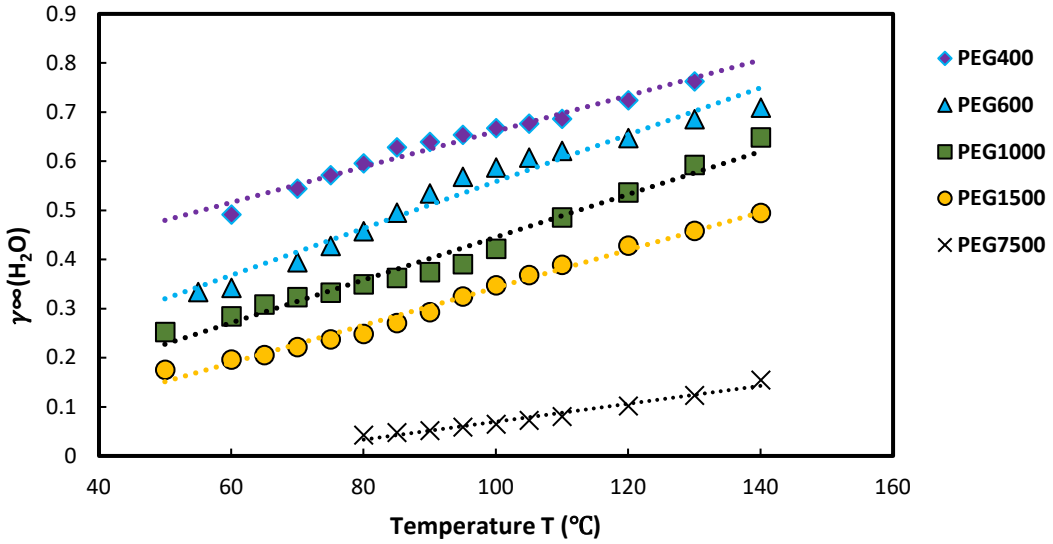


Figure 4. Experimental $\gamma_{H2O,3}^{\infty}$ in several PEGs as function of temperature.[21]

As can be seen in Figure 4, the γ_{13}^{∞} increase with increasing temperature, indicating the weakening of the molecular interactions between PEGs and water. Additionally, as the

molecular weight of PEGs increases the activity coefficient decreases. Under the studied conditions, the activity coefficients were always lower than 1. The PEG with the highest molecular weight has shown the greatest drying capacity per mole, yet the lowest capacity per unit mass. [21]

Sesigur et al.[22] investigated the molecular interactions of PEG400 and tosylate functionalized poly(ethylene glycol) (PEG-Tos) with some nonpolar and polar solvents via inverse gas chromatography, at temperatures ranging from 303 K to 373 K. Thermodynamic parameters such as the weight fraction activity coefficient and the Flory-Huggins polymer-solvent interaction parameters were determined for different solvents. Again the support material used to prepare the stationary phase was Chromosorb-W (AW-DMCS-treated, 80/100 mesh).

The results obtained for $\ln(\gamma_{13}^{\infty})$ are shown in Figure 5 as a function of temperature.

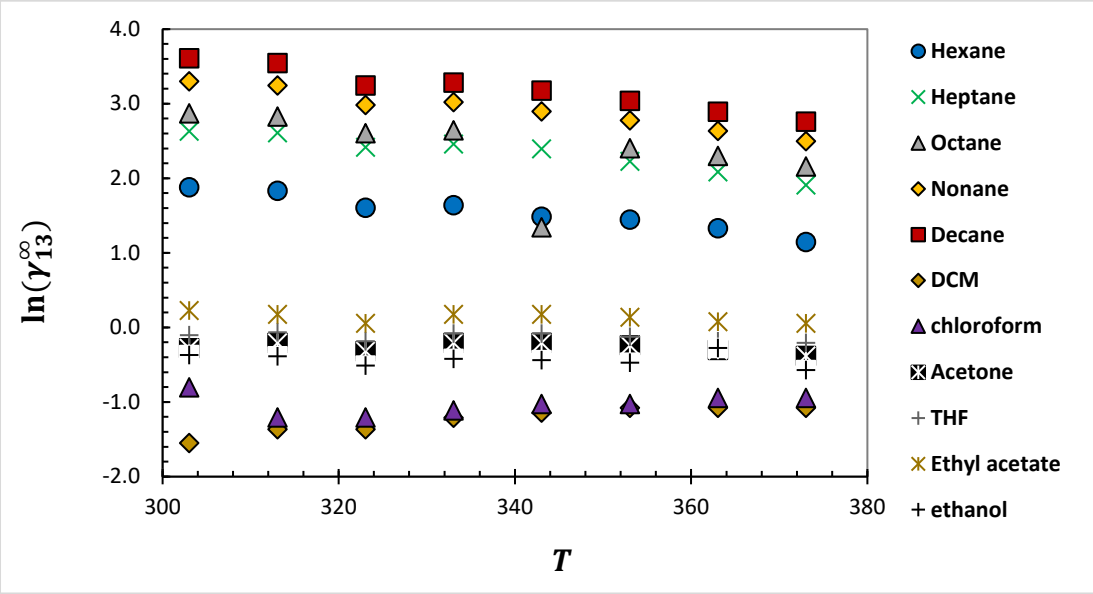


Figure 5. Experimental ln γ_{13}^{∞} of some organic compounds in the PEG-400 as a function of T, reported by Sesigur.[23]

As the temperature increases, the γ_{13}^{∞} values of alkanes decrease, indicating stronger interaction between the solute and solvent. For the other solutes, the change with temperature is less visible. Additionally, the length of the solute chains also plays a role. Figure 5 confirms that when the number of carbon atoms increases in the alkanes, from hexane to decane, the γ_{13}^{∞} values increase, resulting from weaker interactions between the solute and solvent. As expected, polar solutes like dichloromethane (DCM), chloroform, acetone, tetrahydrofuran

(THF), ethyl acetate, and ethanol exhibited lower activity coefficient values compared to alkanes. Ethanol, in particular, showed the lowest value due to the presence of hydrogen bonding.

Humphrey et al.[23] conducted a study on the quantitative determination of cineole in several commercially available essential oils. They found that a flame-ionization detector was particularly effective for quantitative analysis when used with PEG400 as the stationary phase. However, the authors noted potential issues with achieving satisfactory resolution of cineole under these conditions.

Sergey et al.[24] have conducted a study on the separation performance of deep eutectic solvents using inverse gas chromatography, including also PEG-400 as the stationay phase. The stationary phase was prepared using Chromosorb W/AW-DMCS 100/120 mesh as the solid support, with a concentration of non-volatile liquid of 30 % by mass. The samples injected into the GC probes ranged from 0.5 to 2 μL in volume.

The authors[24] measured the γ_{13}^{∞} values of 23 solutes, including aliphatic and aromatic hydrocarbons, alcohols, ketones, ethers, and esters, in mixtures of choline chloride and glycerol with molar ratios of 1:1 and 1:2 using gas−liquid chromatography. The results were compared with the data from Vincent et al.[25] (2012) and Bighi et al. (1969)[26] for PEG400 which are shown in **Figure 6** for various solutes (n-octane, n-decane, n-dodecane, n-tetradecane, benzene, toluene, cyclohexane, methanol, ethanol, propanol, butanol, pentanol). Similar to previous observations, Vincent and Bighi's data indicated that γ_{13}^{∞} values increase with the number of carbon atoms in solute molecules, with alcohols exhibiting lower γ_{13}^{∞} values due to stronger interactions with the solvent. When comparing these results with those obtained by Sergey et al.[24] for choline chloride and glycerol mixtures, it was found that nonpolar aliphatic and aromatic hydrocarbons exhibit much higher γ_{13}^{∞} values in the choline chloride/glycerol mixtures than in PEG400. On the other hand, polar alcohols show strong interactions with the choline chloride/glycerol mixtures, but these γ_{13}^{∞} values remain competitive with those in PEG400, where γ_{13}^{∞} values are typically below unity.

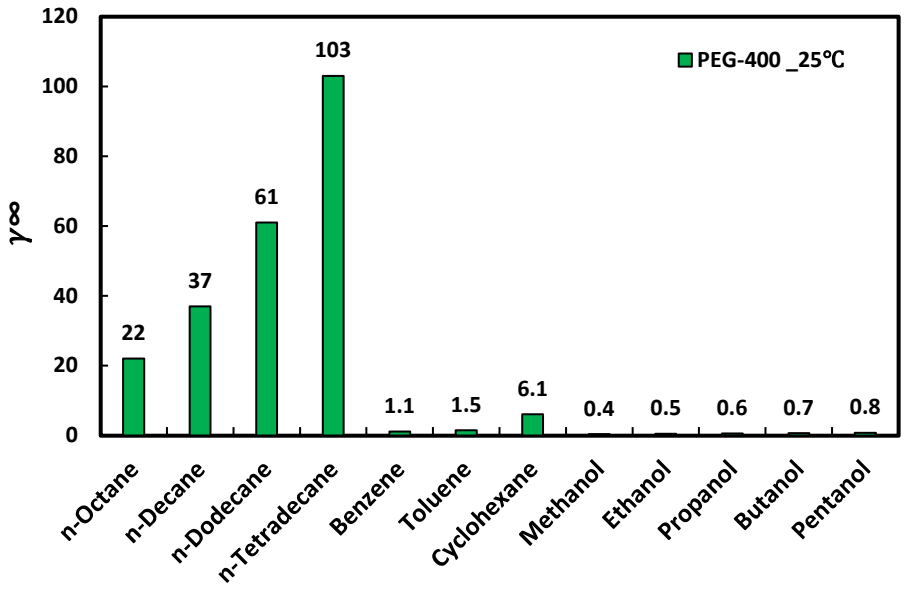


Figure 6. Infinite dilution activity coefficients of n-alcohols and non-polar solutes in PEG-400 at 25 ℃ and 1 bar, reported by Vincent et al. and Bighi et al.[25,26]

Chapter 4. Experimental work

In this work, the infinite dilution activity coefficients will be measured by inverse gas chromatography. A brief description of the technique will be carried out in this chapter.

4.1 Chemicals

The complete list of the organic solutes used in this work can be found in Table A.1 – Appendix A. Additionally, ultrapure water (resistivity of 18.2 MΩ·cm, free particles ≥ 0.22 μm and total organic carbon < 5 $\mu g \cdot dm^{-3}$) was also used. Poly(ethylene glycol) 400 (CAS number 25322-68-3) and 6000 (CAS number 25322-68-3) were procured from Acros Organics.

4.2 Methodologies

4.2.1 FTIR analysis

Fourier transform infrared (FTIR) spectra of the polymers used (PEG400 and PEG6000) were obtained using a Spectrum Two FT-IR Spectrometer da PerkinElmer over the range 450 to 4000 cm^{-1}.

4.2.2 GC analysis

The measurement of the infinite dilution activity coefficients by inverse gas chromatography is a well-established experimental technique.[27,28] The experimental set up available at our research lab will be briefly described in this section.

A Varian 3380 gas chromatograph (**Figure 7**), coupled with a 1041 on-column injector and a thermal conductivity detector (TCD) was used to measure the retention times of the solutes. A glass column with a length of 1 m and an internal diameter of 4 mm, was filled with the desired support (**Figure 8**) and placed in the chromatograph's oven. The filling preparation and the column packing technique were previously described in detail in other publications.[27,28]

Figure 7. Gas chromatograph used in this work.

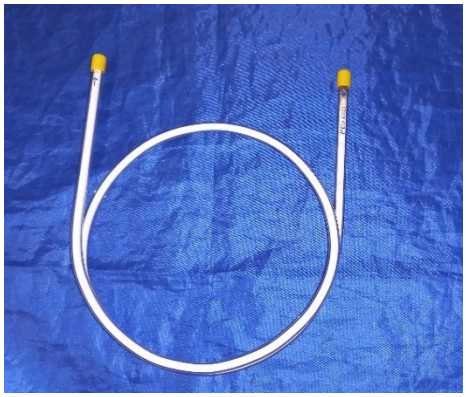


Figure 8. PEG 6000-packed column used in this work.

Before starting the measurements, the columns were pre-conditioned, i.e., a stream of helium gas was pumped through it for at least 6 hours at 393.2 K to aid in the elimination of any impurities. Then, the injector and detector temperatures were set at 503.2 K and 523.2 K, respectively, for the analyses of standard organic solvents and water. Those temperatures were set to 553.2 K and 573.2 K, respectively, for the terpene and terpenoids analyses. The injector was at the setpoint temperature for at least 30 minutes. To assure infinite dilution conditions, a volume range of (0.01-0.3) μL was utilized for injecting the solutes into the column. As a non-retained component, air was also injected together with the organic solute. Two temperatures (343.2 K and 348.2 K) are tipically used for the preliminary trials. Every experiment was always conducted at least in duplicate.

In this work, some preliminary studies were carried out with a column containing 10% in weight of PEG6000. After, the remaining studies were focused on PEG400 for which two columns (1 and 2) were prepared containing 20.44% (w/w) and 30.26% (w/w) of the polymer, respectively.

Chapter 5. Results and discussion

5.1 FTIR analysis

To assess the stability of the stationary phases, both PEG400 and PEG6000 were placed for at least 16 hours at 60ºC in a heating plate. The assay was repeated in 10 K intervals, up to 120 ºC. The spectra of both PEGs were measured at the end of each heating period, and no changes were observed compared to the initial sample. As an example, the spectra obtained for the initial samples of PEG400 is presented in Figure 9.

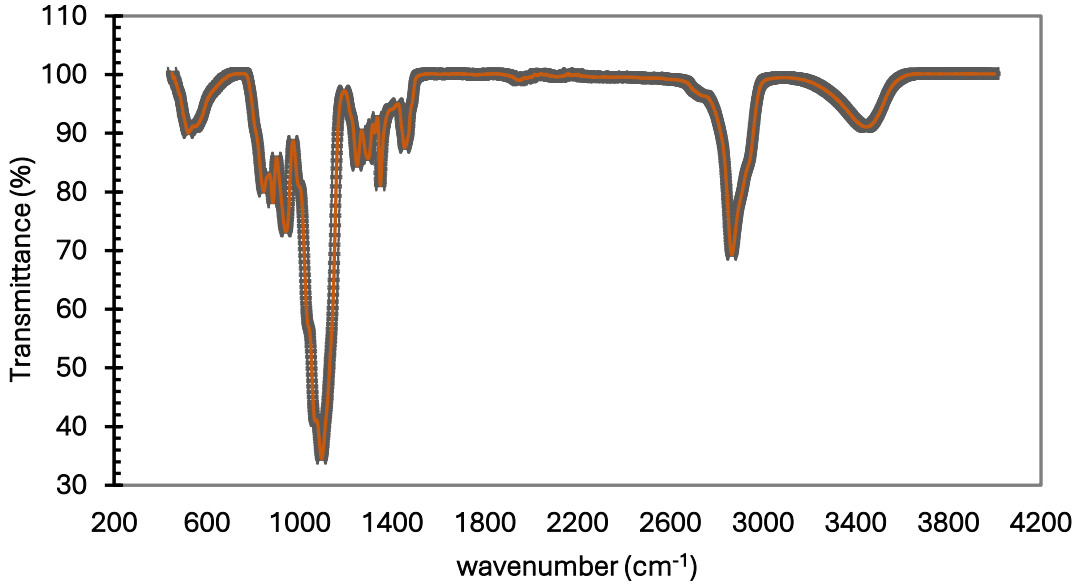


Figure 9. FTIR analysis of the initial sample of PEG400.[29]

Infrared spectroscopy was utilized to analyze the functional groups present in the PEG-400, as shown in **Figure 9.** In the range of 800-900 cm^{-1}, peaks signify stretching vibrations of carbon-carbon (C-C) bonds within the PEG backbone. Next to that, in the range of 1000-1100 cm^{-1}, a specific peak associated with C-O-C stretching vibrations represents the ether linkage (-O-) in the PEG-400 molecule. Following this, in the range of 1100-1200 cm^{-1}, C-O stretching vibrations characteristic of carbon-oxygen bonds within the ether linkages of PEG-400 are observed. In the range of 1300-1400 cm^{-1}, bending vibrations involving carbon-oxygen-hydrogen bonds (C-O-H) occur. Moving further, bending vibrations of C-H bonds are observed around 1400-1470 cm^{-1}, and after that, in the range of 1600-1650 cm^{-1}, the O-H bending vibrations attributed to hydroxyl groups in PEG-400 are evident. In the range of 2800-3000

cm^{-1}, peaks denote stretching vibrations of carbon-hydrogen (C-H) bonds within the PEG-400 backbone. Finally, the peak around 3400 cm^{-1} typically corresponds to the stretching vibrations of O-H bonds.[29]

5.2 Chromatografic experiments

5.2.1 The effect of the injected volume in PEG6000 stationary phase

In previous works using ILs as stationary phases, the injection volume was 0.3 μL. As in this work the stationary phase started to be PEG6000, with higher molecular weight, and to ensure infinite dilution conditions (in the mole fraction scale) the effect of the volume of solute injected on the activity coefficients was studied.

In the first set of assays, the effect of changing the volume of injected solute was evaluated for 10 model compounds (octane, cyclohexane, THF, acetone, methyl acetate, acetonitrile, ethanol, 2-propanol, α-pinene and β-pinene). Three volumes of solute were injected (0.3, 0.1, and 0.01 μL) at 70°C. The results are presented in **Figure 10**.

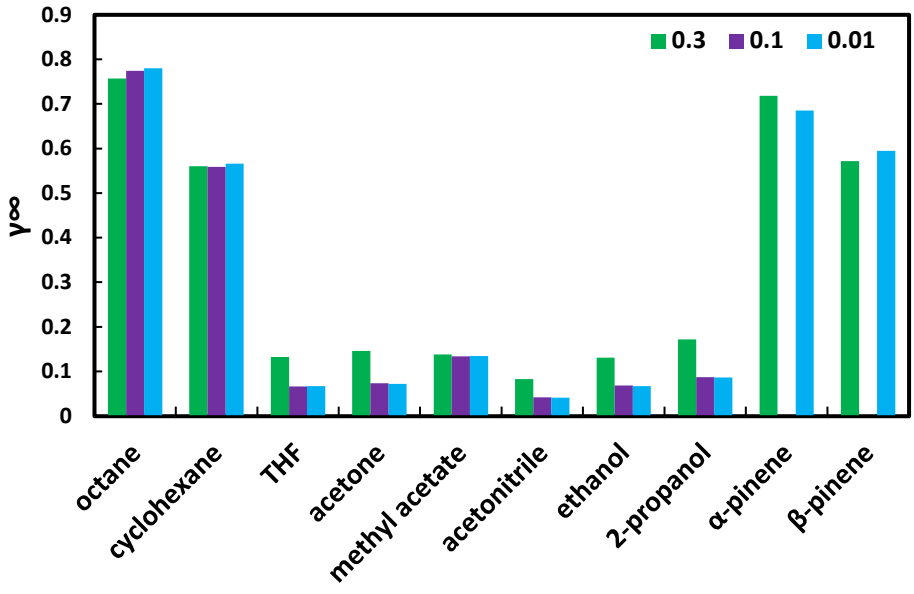


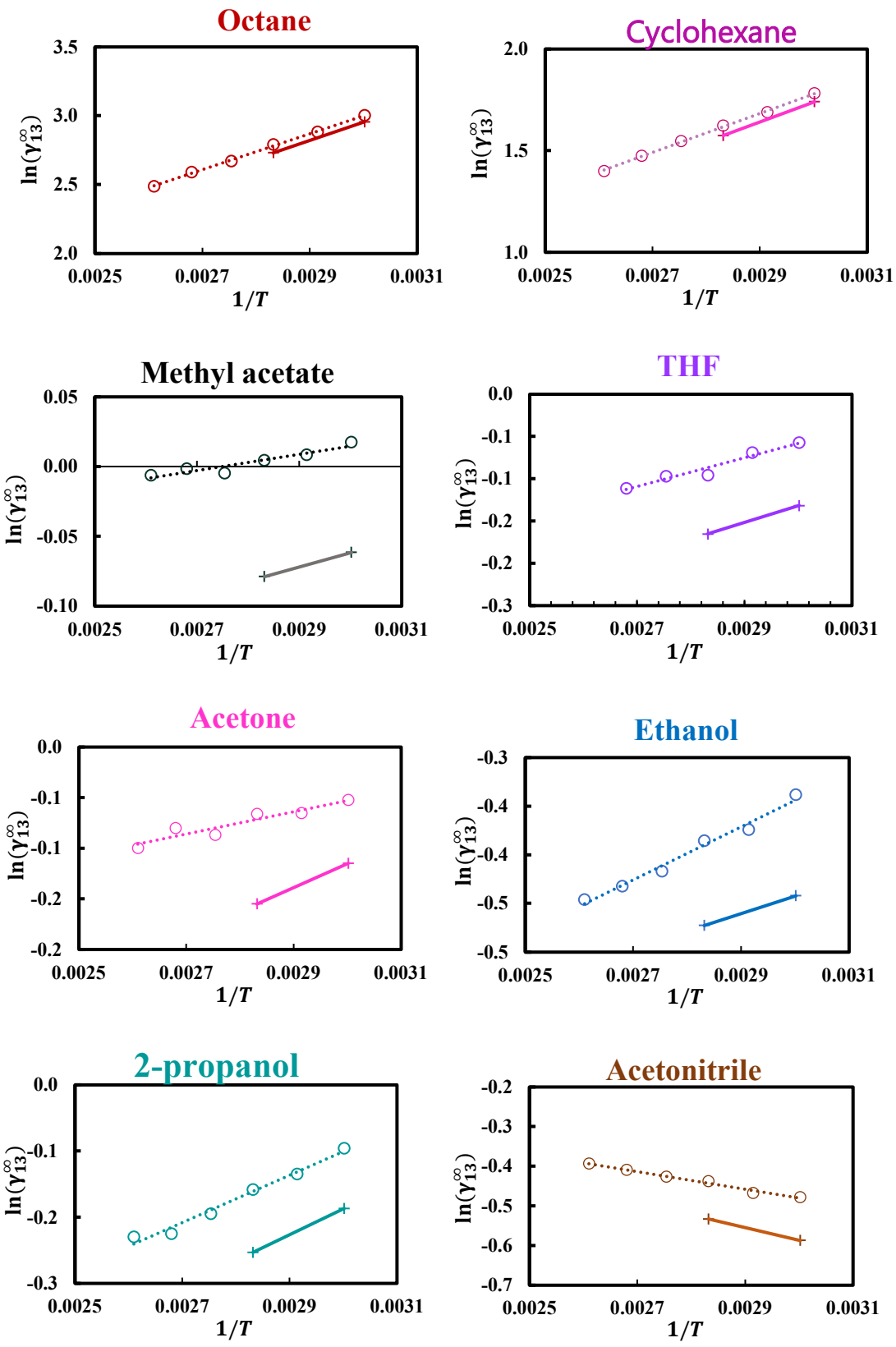
Figure 10. Infinite dilution activity coefficients of selected solutes in PEG6000, calculated from the retention volumes obtained using different injection volumes (0.3, 0.1, and 0.01 μL) at 70 °C.

For the lower molecular weight THF, acetone, acetonitrile, ethanol, and 2-propanol there was a reduction in the values of the activity coefficients when the injected volume decreased from 0.3 to 0.1 μL. Further reducing the injected volume to 0.01 μL did not produce significant changes. The results obtained also allowed us to have a first estimate of the separation factors of the binary mixture α-pinene/β-pinene, at 70°C: selectivity $S_{ij}^{\infty} = 1.20$, capacity ($k_j^{\infty} = 1.67$) and solvent performance index ($Q_{ij}^{\infty} = 2.0$). These findings suggest further studies of this family of solvents to address the separation of α-pinene and β-pinene, among other mixtures. In the remaining work, PEG400 was selected due to its much lower melting point which extends the range of application of this family of compounds.

5.2.2 Comparison between two columns containing PEG400

In this set of experiments, PEG-400 was selected as the stationary phase to assess the impact of the solvent on the interactions of terpenes, terpenoids, and various organic solutes using gas chromatography (GC) to measure the infinite dilution activity coefficients for each solute. Two columns were independently prepared with different amounts of stationary phase: column 1 contained 20% in weight of PEG400, and column 2 contained 30%. The study compared the results from these two columns across 14 solutes: octane, cyclohexane, methyl acetate, THF, acetone, ethanol, 2-propanol, acetonitrile, eucalyptol, fenchone, pinene, β-pinene, p-cymene, and limonene.

Due to some experimental constraints (the second column started unpacking), it was not possible to complete all the predicted assays in the second column. The first column provided measurements at temperatures ranging from 60 to 120 °C, with some solutes having incomplete data (e.g., α-pinene, β-pinene, and p-cymene at 120 °C; eucalyptol and fenchone lacking data at 60, 70, and 120 °C; and limonene only at 60 °C). The second column recorded results at 60 and 80 °C. The results obtained using both columns are depicted in **Figure 12.**


Octane
Cyclohexane
Methyl acetate
THF
Acetone
Ethanol
2-propanol
Acetonitrile
$\ln(\gamma_{13}^{\infty})$
$1/T$
0.0025
0.0027
0.0029
0.0031

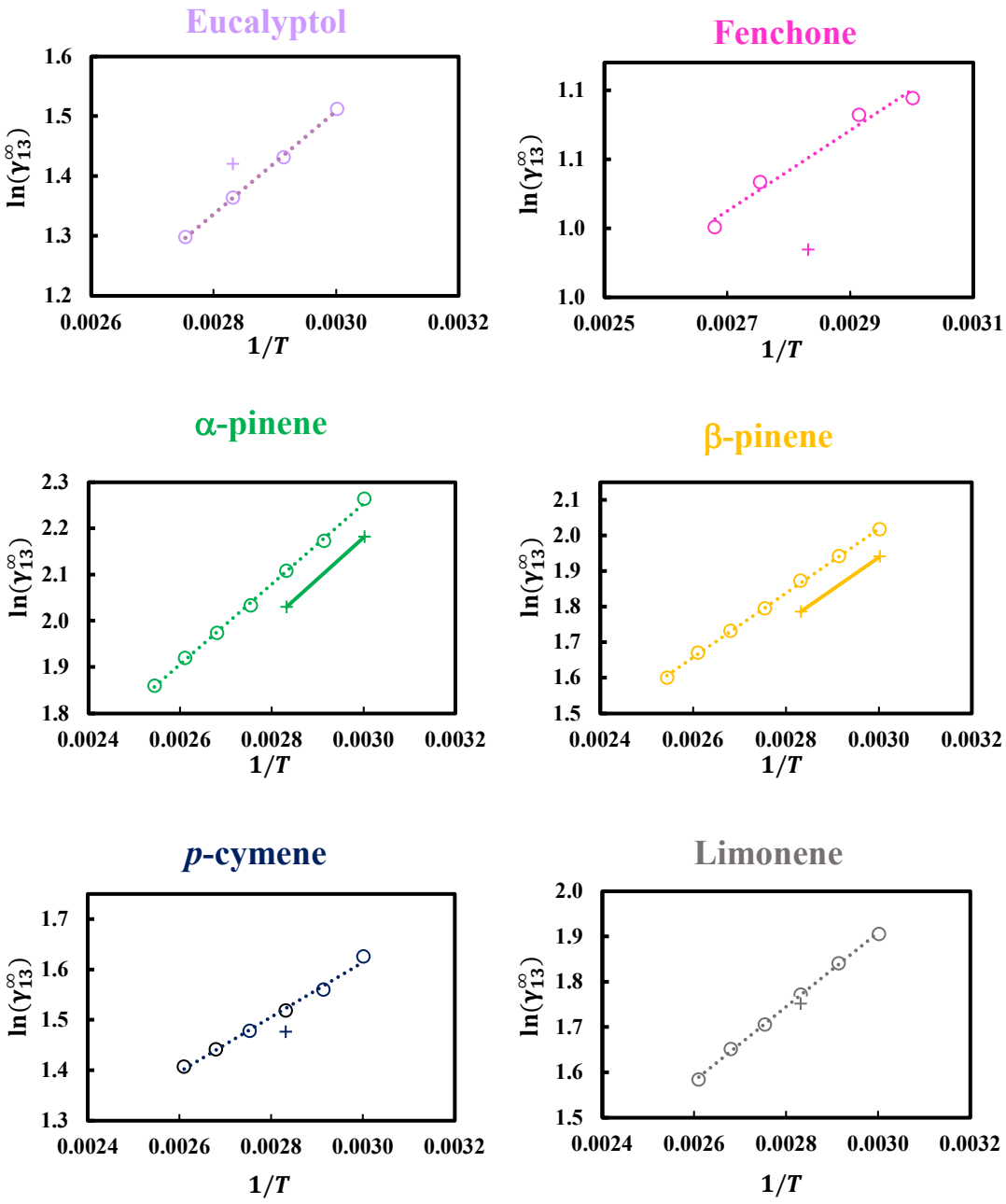


Figure 11. Experimental ln γ_{13}^{∞} of 14 organic solutes as function of $1/T$ obtained in two columns of PEGs-400: open circles - first column; crosses - second column.

With the exception of eucalyptol, the infinite dilution activity coefficients obtained in the second column were lower than those in the first column.

The linear plots of ln (γ_{13}^{∞}) versus $1/T$ of all solutes present a consistent trend of decreasing γ_{13}^{∞} with increasing temperature, with the exception of acetonitrile that displayed the inverse slope. When at least 2 datapoints were available for a given solute, the data slopes were consistent among columns.

Acetone, ethanol, and 2-propanol demonstrate lower $\ln(\gamma_{13}^{\infty})$ values compared to non-polar solutes, reflecting their higher solubility and better interactions with PEG400. When comparing the two PEG400 columns, the trends are consistent, though slight differences are observed. Acetonitrile, with intermediate $\ln(\gamma_{13}^{\infty})$ values, confirms its moderate polarity and interaction strength.

For terpenes and terpenoids, including compounds like α-pinene, β-pinene, p-cymene, limonene, eucalyptol, and fenchone, the observed trends confirm a consistent pattern of increased solubility with increasing temperature.

To better quantify the differences observed, **Table 3** presents the relative errors (RE%) for the infinite dilution activity coefficients (γ_{13}^{∞}) between the two PEG-400 columns at 80 °C, calculated using the following equation:

$$\text{RE (\%)} = \left| \frac{(\gamma_{13}^{\infty})\text{col\_1} - (\gamma_{13}^{\infty})\text{ col\_2}}{(\gamma_{13}^{\infty})\text{ col\_2}} * 100 \right| \quad (11)$$

Table 3. Relative error (RE) in γ_{13}^{∞} obtained in columns 1 and 2, at 80 ºC.

Solute	RE (%)
Octane	6.2
Cyclohexane	5.0
Methyl acetate	8.7
THF	7.2
Acetonitrile	10.0
Acetone	9.3
Ethanol	9.1
2-propanol	10
α-pinene	8.1
β-pinene	9.0
Limonene	9.3
p-cymene	8.6
Eucalyptol	9.6
Fenchone	10.2

Smaller non-polar compounds such as octane and cyclohexane displayed relative errors of 6.2% and 5.0%, respectively. For the more polar components and higher molecular weight

terpenes, the relative errors are more pronounced with a maximum value of 10%. These moderately high RE% values imply that one (or both) columns may not be accurately predicting the interactions of these solutes with PEG-400, suggesting that further studies should be carried out in the future in a third column.

5.2.3 Infinite dilution activity coefficients

In this study, temperature is a important factor affecting the infinite dilution activity coefficients, and process design. The following plots illustrate how the natural logarithm of the infinite dilution activity coefficients varies with the inverse of absolute temperature. This relationship is typically linear, as shown by Equation (5), showing either an increase or decrease depending on the interactions of the solute with PEG-400 as the stationary phase. In this section, we analyze the results from the first column, which was studied at temperatures ranging from 60 to 120 ℃, divided according to the solutes' chemical families. The complete γ_{13}^{∞} and capacity data are reported in Tables B1 and B2 of Appendix B.

Figure 12 represents the plots for heptane, octane, nonane, decane, and cyclohexane in PEG-400. As can be seen, a straight line is obtained for each solute, meaning their activity coefficients change predictably with temperature. Among the common organic solutes studied in this work, alkanes present the highest positive $\ln(\gamma_{13)}^{\infty}$ which increase linearly with $1/T$. As the number of carbons increases, γ_{13}^{∞} also increases.

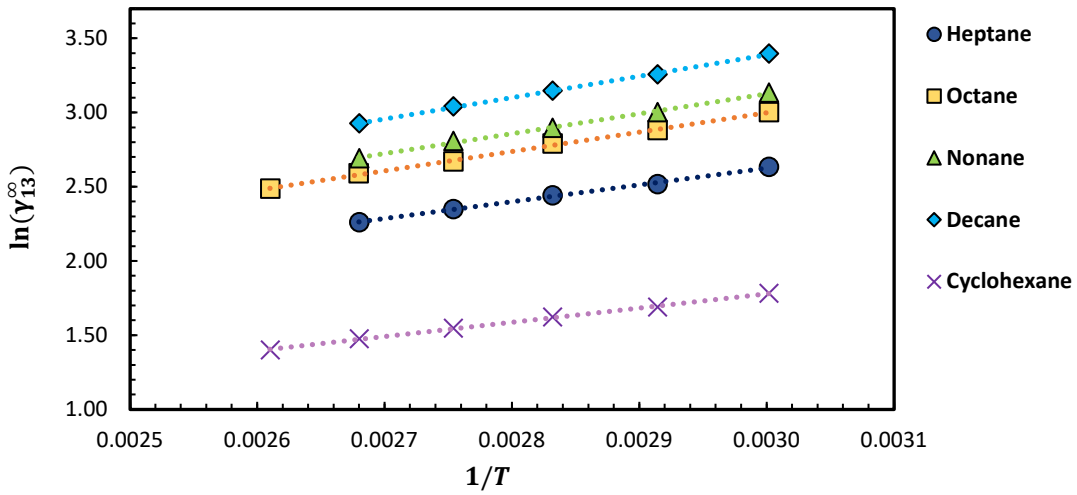


Figure 12. Experimental ln γ_{13}^{∞} of alkanes and cyclohexane in PEG-400 as a function of $1/T$.

The esters (methyl acetate, ethyl acetate, and vinyl acetate) present distinctive behavior in their infinite dilution activity coefficients (γ_{13}^{∞}) across the range of temperatures studied, as illustrated in **Figure 13**. Methyl acetate shows γ_{13}^{∞} values close to one indicating nearly ideal behaviour. Ethyl acetate and vinyl acetate demonstrate a consistent decrease in γ_{13}^{∞} with increasing temperature, similar to the trends observed for alkanes and cyclohexane. However, their γ_{13}^{∞} values are generally lower than those of the alkanes, suggesting more ideal behavior. This behavior can be attributed to the polar nature of ester functional groups, which enhances their solubility in PEG compared to nonpolar alkanes.

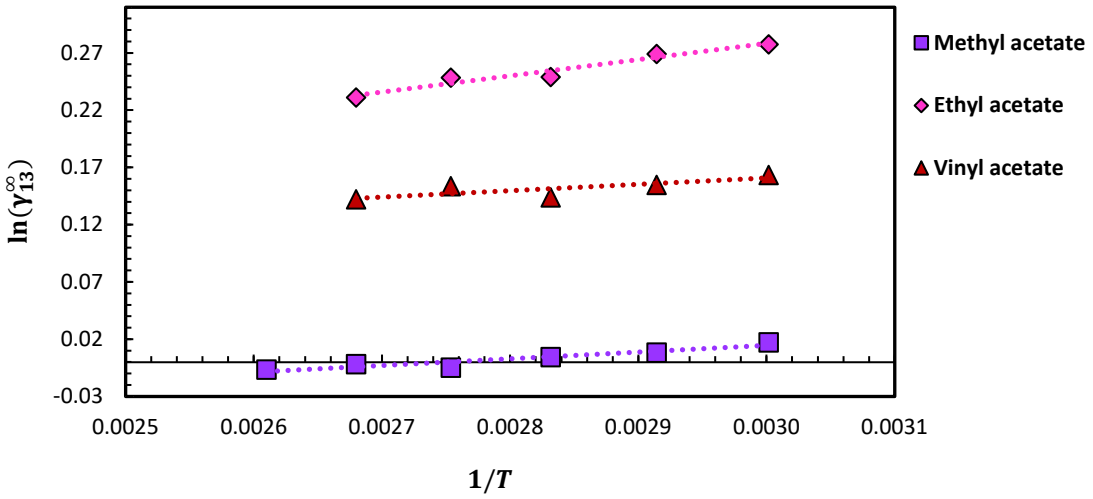


Figure 13. Experimental ln γ_{13}^{∞} of the esters in PEG-400 as a function of T^{-1}.

As show in **Figure 14** the ethers (THF, 1,4-dioxane, and diethyl ether) also have lower γ_{13}^{∞} than alkanes, following their polarity trend. Tetrahydrofuran (THF) has slightly negative ln(γ_{13}^{∞}) values, which decrease with increasing temperature, indicating favorable interactions with the solvent. A similar behaviou is observed for the most polar 1,4-dioxane that shows the lowest γ_{13}^{∞} (< 1). On the other hand, the only studied acyclic ether and the more apolar, diethyl ether, has γ_{13}^{∞} > 1.

Figure 15 shows the results obtained for acetone (γ_{13}^{∞} < 1) and 2-butanone (γ_{13}^{∞} > 1) which remain close to ideality. On the other hand, acetonitrile displays an increasing trend in γ_{13}^{∞} values as temperature increases, and γ_{13}^{∞} lower than 1 which can be an useful indicator for the use of PEG400 to remove nitrogen compounds from fuels. Further assays should be carried out with other nitrogen-containing compounds.

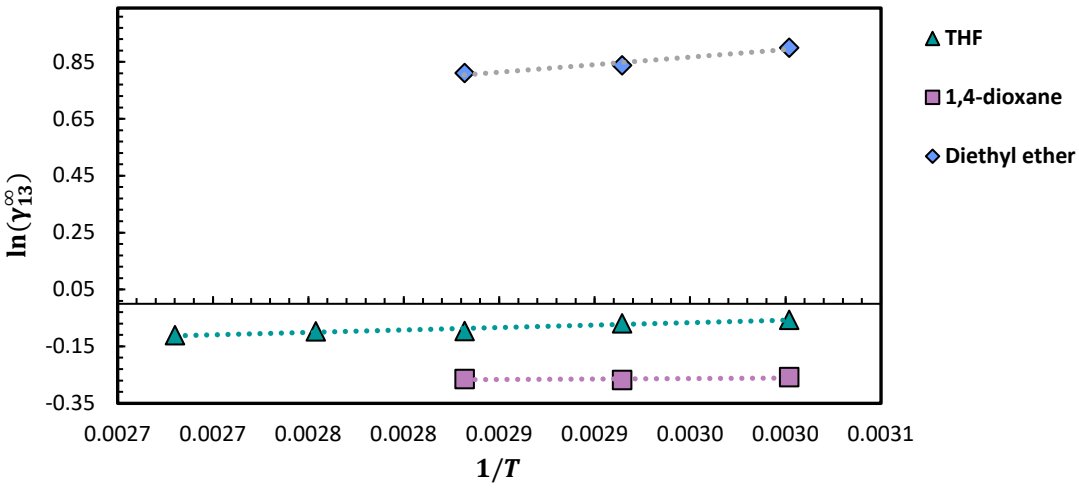


Figure 14. Experimental ln γ_{13}^{∞} of the ethers in PEG-400 as a function of T^{-1}.

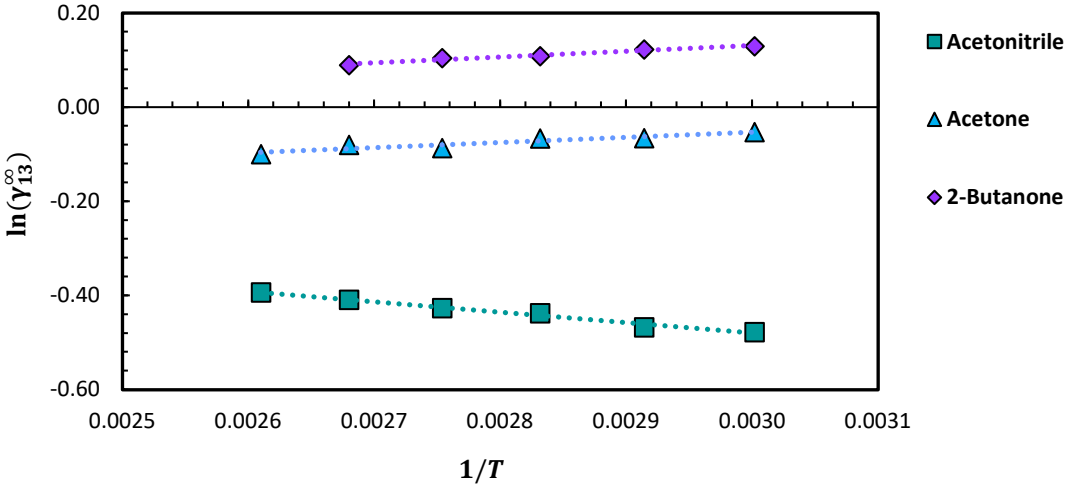


Figure 15. Experimental ln γ_{13}^{∞} of acetonitrile and two ketones in PEG-400 as a function of T^{-1}.

Figure 16 shows the results obtained with the more polar solutes water and alcohols, capable of establishing cross association with the ether bond in PEG. Water has the lowest $\ln(\gamma_{13}^{\infty})$ values than any other solute in PEG-400 which was expected indicating very favorable solute-solvent interactions. Regarding alcohols, in general, the γ_{13}^{∞} values increase with increasing

number of carbon atoms in the alkyl chain. Only for *tert*-butanol, there are positive deviations to ideality. The $\ln(\gamma_{13}^{\infty})$ increases with $1/T$ for all solutes except methanol.

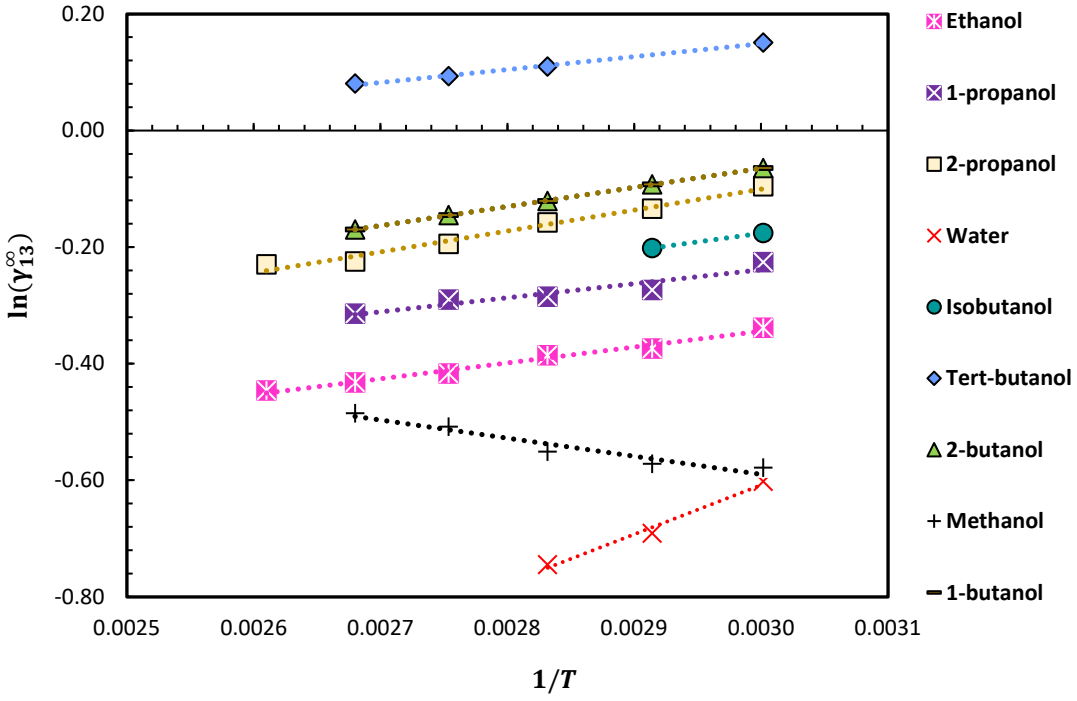


Figure 16. Experimental ln γ_{13}^{∞} of water and alcohols in PEG-400 as a function of T^{-1}.

Besides water and common organic solvents, various terpenes and terpenoids were also studied and the results obtained are shown in Figures 17 to 20. The plots expose a consistent trend where $\ln(\gamma_{13}^{\infty})$ decreases with decreasing inverse temperature (increasing temperature) for most compounds, indicating increasing solubility with higher temperatures. Among the hydrocarbon terpenes, all present large positive deviations to ideality similarly to alkanes and cyclohexane. In general α-pinene presents the highest $\ln(\gamma_{13}^{\infty})$ values, suggesting it is the least soluble, while *p*-cymene shows the lowest values. The intermediate behavior of β-pinene, limonene, myrcene, and γ-terpinene is shown by their respective $\ln(\gamma_{13}^{\infty})$ values.

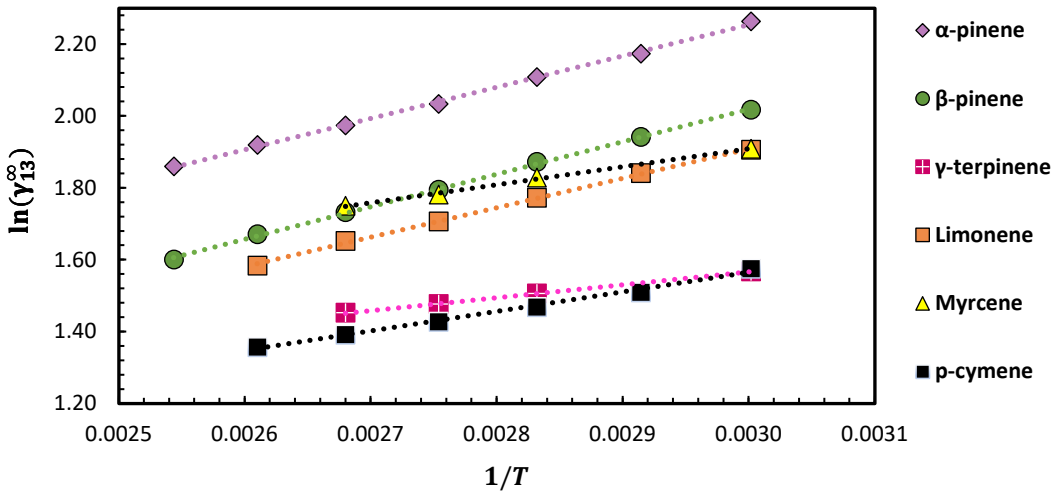


Figure 17. Experimental ln γ_{13}^{∞} of terpenes in PEG-400 as a function of T^{-1}.

As expected, the low polarity ether terpenoids (**Figure 18**) showed a higher interaction with PEG-400 than terpenes. For eucalyptol, $\ln(\gamma_{13}^{\infty})$ decreased from 1.51 to 1.30 as the inverse temperature decreases, indicating improved solubility with increasing temperature. Eucalyptol has higher $\ln(\gamma_{13}^{\infty})$ values compared to α-pinene oxide, at 110°C.

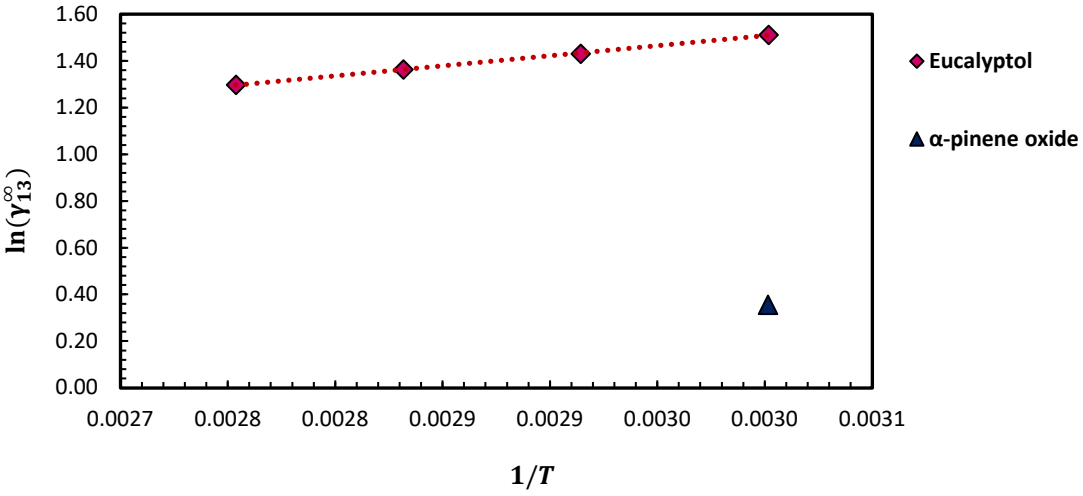


Figure 18. Experimental ln γ_{13}^{∞} of ether terpenoids in PEG-400 as a function of T^{-1}.

The results presented in **Figure 19** are for ketone terpenoids. They present higher molecular weight and more nonpolar character than the common ketones previously studied (acetone and butanone) that result in higher positive deviations to ideality.

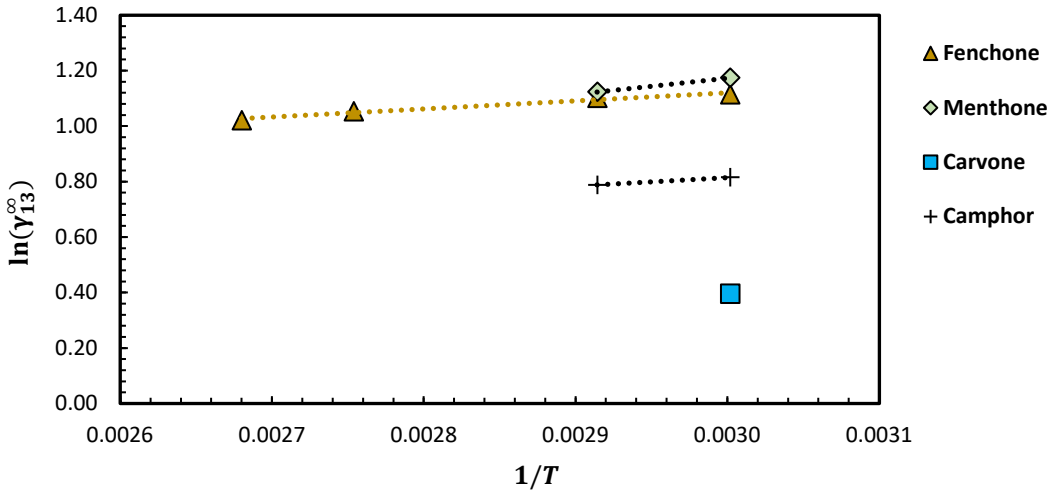


Figure 19. Experimental ln γ_{13}^{∞} of ketone terpenoids in PEG-400 as a function of T^{-1}.

Based on the results presented in **Figure 20**, the ln(γ_{13}^{∞}) for citronellol, linalool, borneol, and menthol in PEG-400 are also positive and close to the values obtained for most ether and ketone terpenoids. This contrasts with the negative deviations to ideality observed for most of the lower molecular weight counterparts shown in Figure 16. Nevertheless, the differences found between the γ_{13}^{∞} of hydrocarbon terpenes and terpenoids suggest additional studies in a wider temperature range.

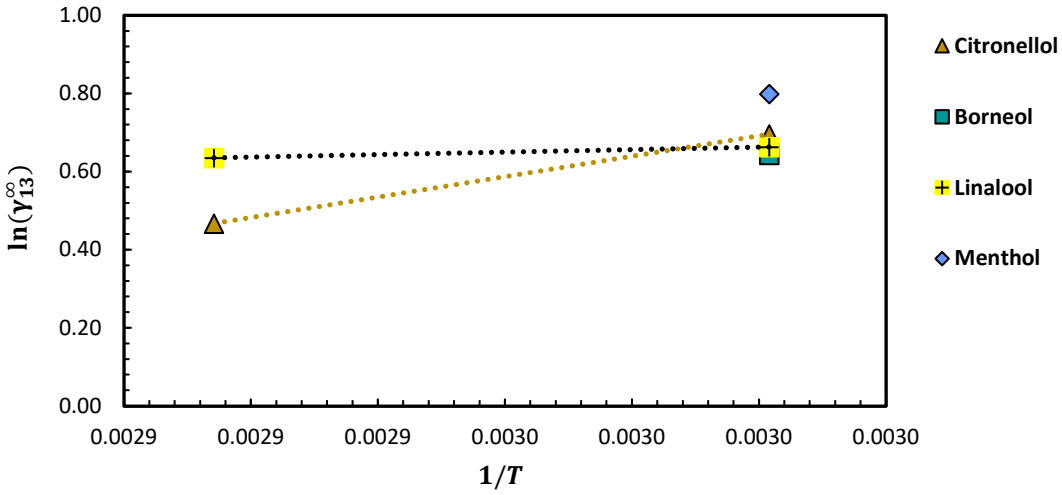


Figure 20. Experimental ln γ_{13}^{∞} of alcohol terpenoids in PEG-400 as a function of T^{-1}.

5.2.4 Comparison with literature data

In this section, a comparative analysis of the γ_{13}^{∞} measured in this work and found in the literature will be carried out for various solutes, including alkanes, ethers, esters, ketones, acetonitrile, water, and alcohols, in PEG-400. Again, the experimental data was plotted as the logarithm of the infinite dilution activity coefficients against the inverse of temperature in **Figures 21 to 25**. The literature results were collected from Sesigur et al. (2016), Bestani et al. (1989), and Castello (1977). In general, the results obtained in this work show a moderate consistency with literature data, being systematically higher for all solutes with the exception of the data set of water. In general, the $\ln(\gamma_{13}^{\infty})$ data versus T^{-1}, measured by Sesigur et al. (2016), has a poorer linear fit. A more detailed analysis will be performed next for each family of compounds.

As can be seen in **Figure 21**, the same γ_{13}^{∞} ranking from heptane to decane is obtained in all sets of data, as well as the same behaviour with temperature. When compared with literature data, higher $\ln(\gamma_{13}^{\infty})$ values were obtained in this work. For octane and decane, the data from Sesigur et al. (2016) and Castello (1977) are closer to each other, then to the data measured in this work.

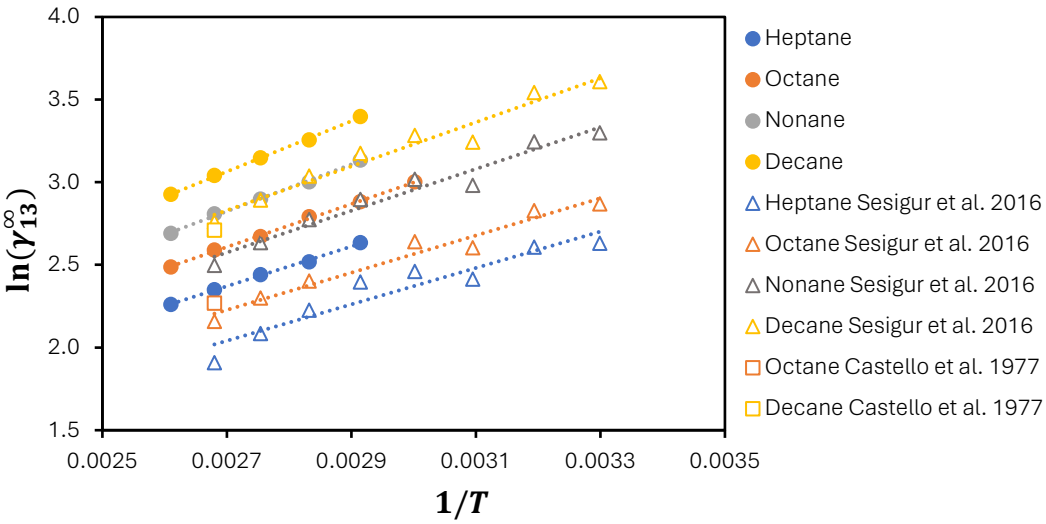


Figure 21. Comparison between the ln (γ_{13}^{∞}) of alkanes in PEG-400: open triangles - literature data; full circles - this work.

The comparison of the experimental results obtained in this work with literature data from Sesigur et al. (2016) is demonstrated in **Figures 22** and **23** for ethyl acetate and tetrahydrofuran.

In all datasets, $\ln(\gamma_{13}^{\infty})$ decreases with increasing temperature, but the values measured in this work present a more linear trend, though higher values than literature. Positive and negative deviations are obtained for ethyl acetate and THF, respectively, for both data sets (literature and this work).

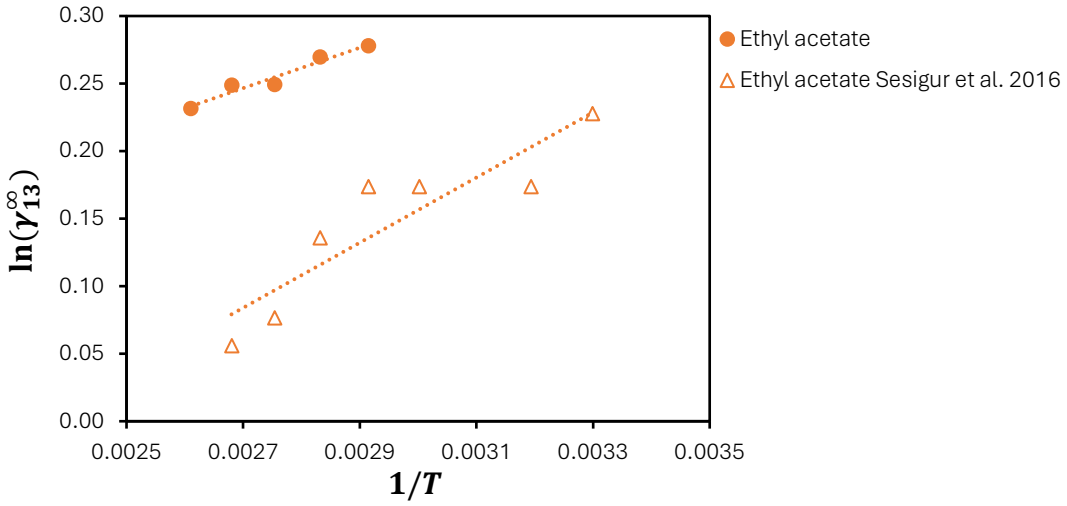


Figure 22. Comparison between the $\ln(\gamma_{13}^{\infty})$ of ethyl acetate in PEG-400: open triangles - literature data; full circles - this work.

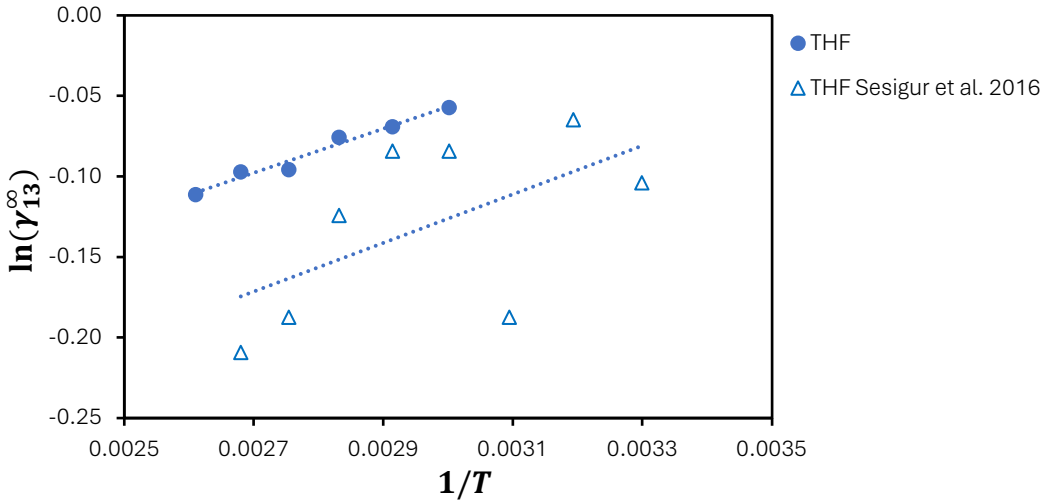


Figure 23. Comparison between the ln (γ_{13}^{∞}) of tetrahydrofuran in PEG-400: open triangles - literature data; full circles - this work.

Figure 24 presents the $\ln(\gamma_{13}^{\infty})$ values for acetone and water, comparing the experimental data obtained in this work to the data reported by Sesigur et al. (2016), Bestani et al. (1989), and Castello (1977). For acetone, our experimental results showed that the $\ln(\gamma_{13}^{\infty})$ values

remained relatively constant with increasing temperature, ranging from -0.05 at 343.2 K to -0.10 at 383.2 K. This indicates that the interactions between acetone and PEG-400 are relatively temperature-independent in our experimental setup. Compared to Sesigur et al., our $\ln(\gamma_{13}^{\infty})$ values were again higher.

For water, we compared our results with the data from Bestani et al. (1989). As can be seen, though both predict negative deviations to ideality, the variation of $\ln(\gamma_{13}^{\infty})$ follows opposite trends. Further assays should be carried out in a wider temperature range.

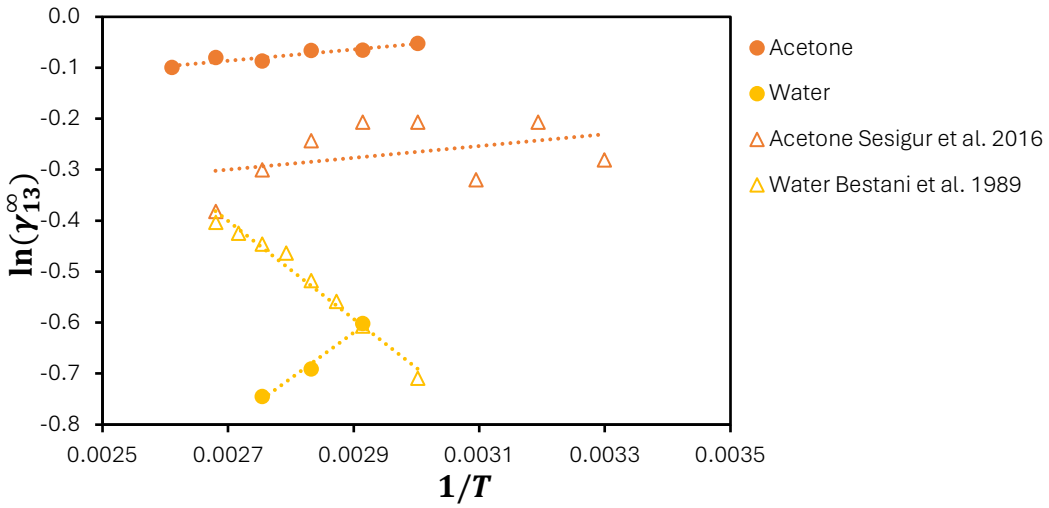


Figure 24. Comparison between the $\ln(\gamma_{13}^{\infty})$ of water and acetone in PEG-400: open triangles - literature data; full circles - this work.

Figure 25 illustrates a data comparison of the γ_{13}^{∞} of various alcohols, namely methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol. The three sets of data show that all alcohols present negative deviations to ideality, though the values measured in this work are closer to ideality. The same γ_{13}^{∞} ranking is obtained in this work and by Castello (1977).

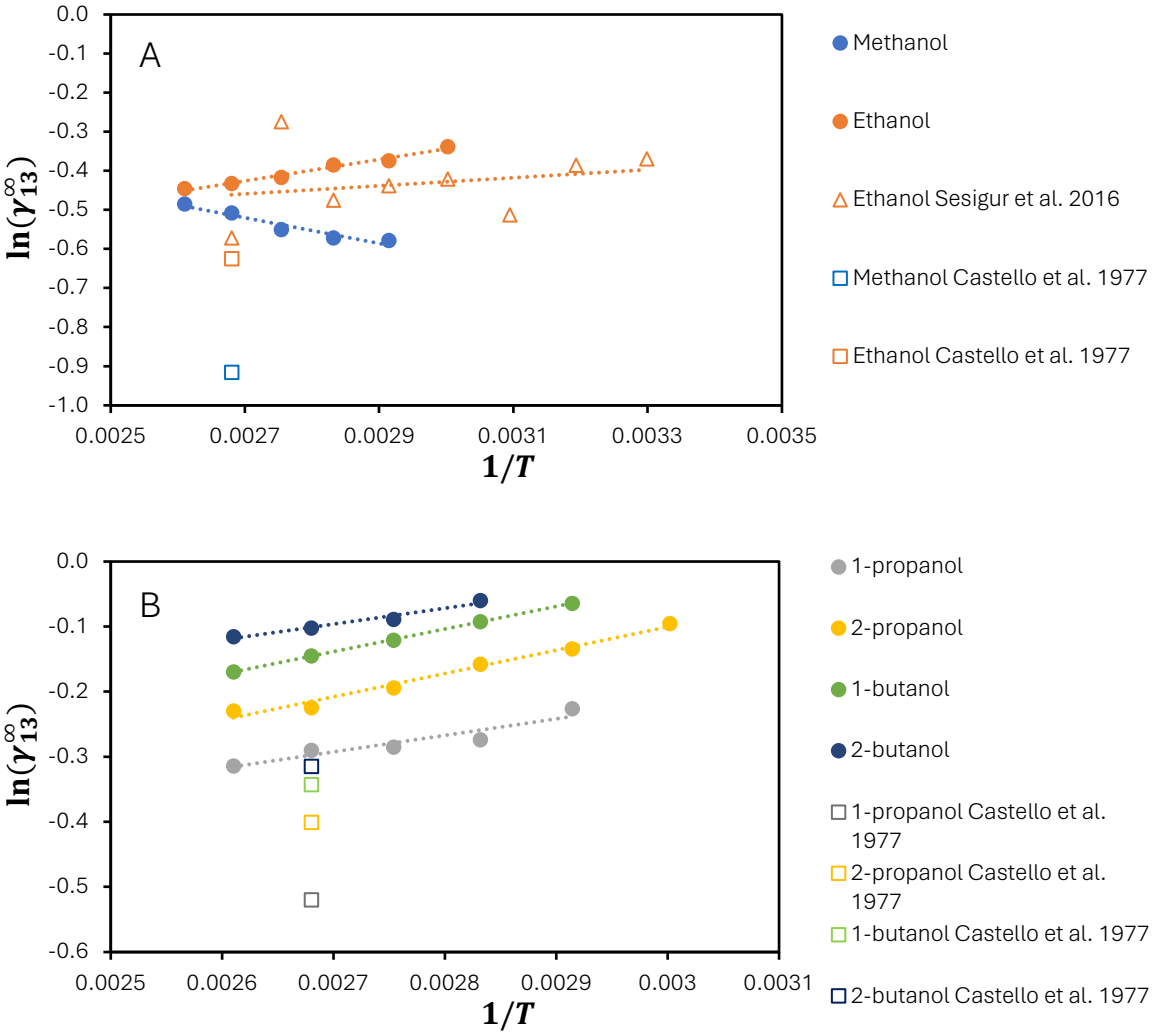


Figure 25. Comparison between the ln (γ_{13}^{∞}) of alcohols in PEG-400: open symbols - literature data; full circles - this work.

The comparative analysis performed in this section reinfornces the need to perform future studies in a third column.

5.2.5 Selectivities and capacities

To evaluate the effectiveness of PEG-400 as a solvent for various separation challenges involving homogeneous binary mixtures, it is essential to determine the fractionation factors. Key metrics such as selectivities (S_{ij}), capacities (K_j), and solvent performance indexes (Q_{ij}) for the mixtures under study were derived from the γ_{13}^{∞} values, as shown in Equations 8-10. A solvent is considered effective for fractionation when it exhibits high selectivities and capacities, as low S_{ij} values lead to poor separation efficiency, and low K_j values indicate weak solute-solvent affinity, resulting in larger solvent volumes for separation. This research

explored the capabilities of PEG-400, specifically in terms of S_{ij}, K_j, and Q_{ij}, for processing critical separation tasks such as separation of terpenic mixtures. Detailed discussions on each type of separation problem are provided below.

5.2.6 Fractionation of terpenes mixtures

In this section, we highlight the performance index (Q_{ij}) of PEG-400 and its capacity (K_j) to separate various binary terpene mixtures, including limonene + carvone, limonene + linalool, menthone + menthol, borneol + camphor, α-pinene + β-pinene, α-pinene + limonene, and *p*-cymene + limonene. We compare these results with the performance index and capacity of ionic liquids at 403.2 K, as reviewed by Zambom *et al.*[15]. The following Figures 26 to 28 present this comparison: the binary mixtures α-pinene + β-pinene, α-pinene + limonene, and *p*-cymene + limonene include the performance index and capacity of PEG-400 at 393.15 K, while the other mixtures include these metrics for PEG-400 at 383.15 K.

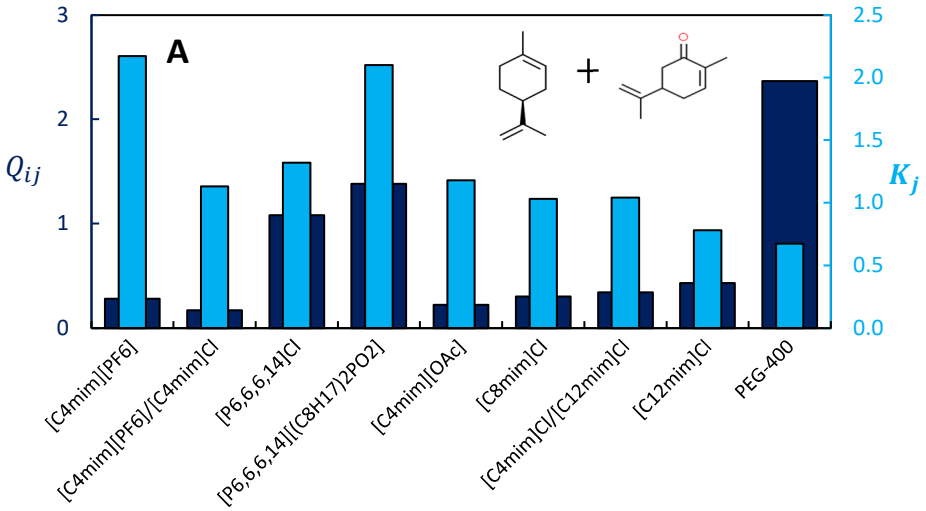


Figure 26. Experimental capacity and solvent performance index of PEG-400 at 383.15 K and ionic liquids at 403.15 K for binary mixtures of limonene + carvone (**A**).

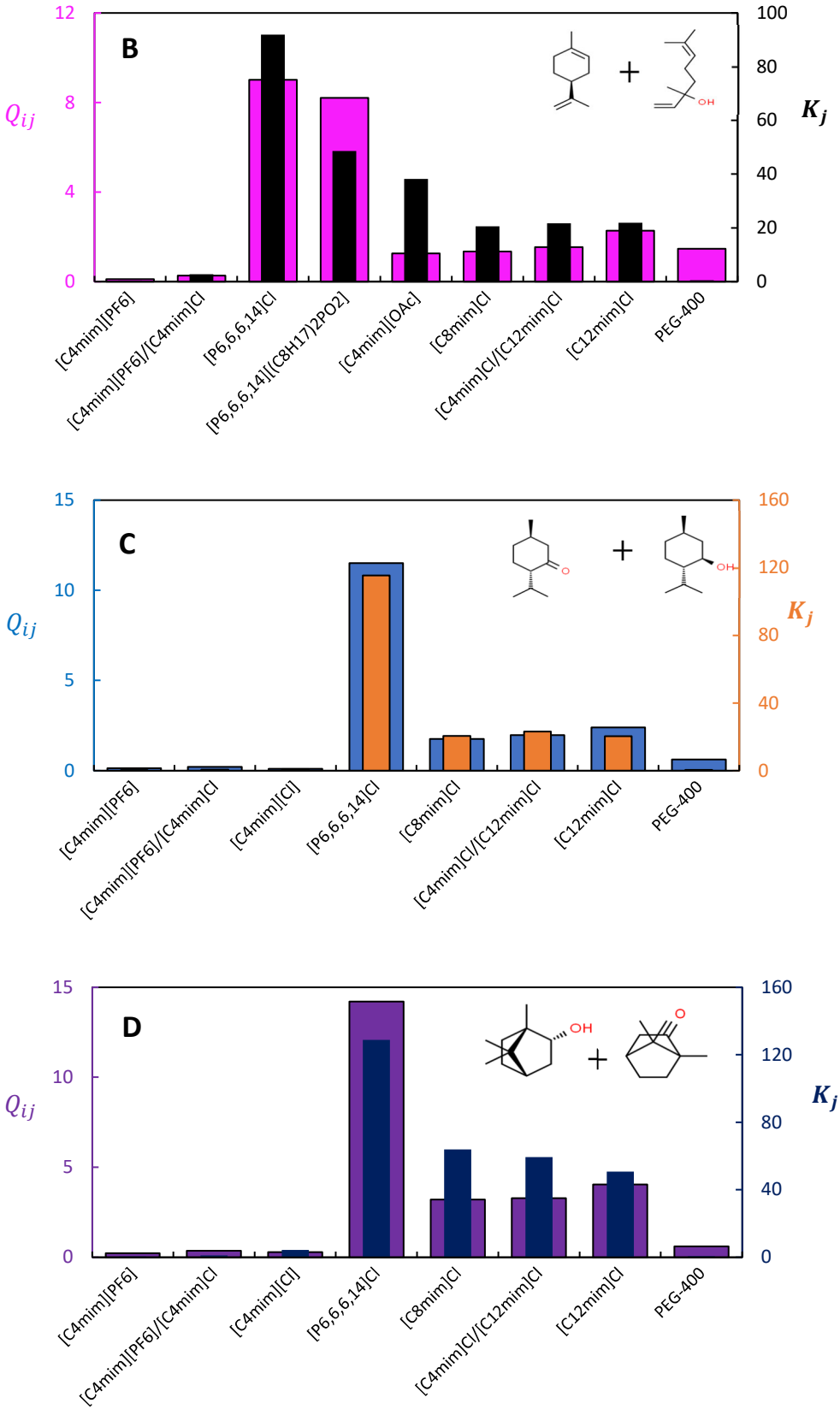


Figure 27. Experimental capacity and solvent performance index of PEG-400 at 383.15 K and ionic liquids at 403.15 K for binary mixtures of limonene + linalool (**B**), menthone + menthol (**C**), borneol + camphor (**D**).

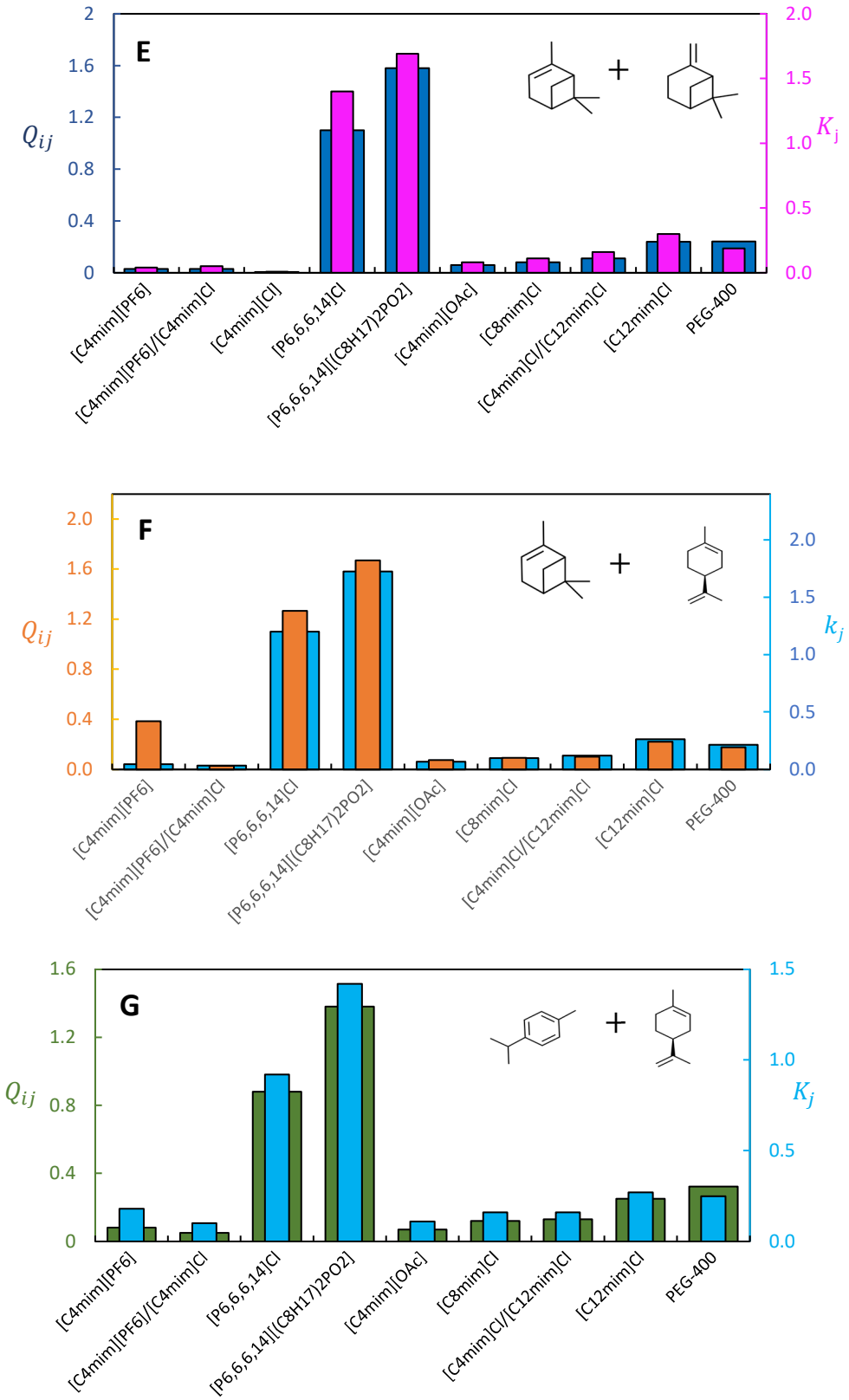


Figure 28. Experimental capacity and solvent performance index of PEG-400 at 383.15 K and ionic liquids at 403.15 K for binary mixtures of α-Pinene + β-Pinene (**E**), α-Pinene + Limonene (**F**), and *p*-Cymene + Limonene (**G**).

As can be seen in **Figure 26** (**A**), PEG-400 demonstrates the superior efficiency for the separation of limonene and carvone at 383.15 K, with the highest index of performance (Q_{ij} = 2.37), though its capacity (0.67) is moderate compared to other solvents. Another solvent can be highlighted, $[P_{6,6,6,14}][(C_8H_{17})_2PO_2]$, that also performs well, balancing good performance and capacity.

Based on the comparative plots for each binary mixture, $[P_{6,6,6,14}]Cl$ stands out across all three plots in **Figure 27**, demonstrating exceptional performance for separating limonene + linalool (**B**), menthone + menthol (**C**), and borneol + camphor (**D**). It achieves the highest indices of performance (9.0, 11.5, 14.2) and capacities (91.9, 115.4, 128.8), making it the most efficient solvent overall. In Plot **B**, PEG-400 shows good efficiency for limonene + linalool with a solvent performance index of 1.46 but its capacity (0.53) is relatively low. Other notable solvents for this mixture include $[P_{6,6,6,14}][(C_8H_{17})_2PO_2]$ and $[C_{12}mim]Cl$, which balance high efficiency and capacity. In Plot **C**, for menthone + menthol, PEG-400's performance is lower (Q_{ij} = 0.62, capacity 0.45), whereas solvents like $[C_{12}mim]Cl$ and $[C_8mim]Cl$ show better balance between efficiency and capacity. In Plot **D**, for borneol + camphor, PEG-400 shows lower performance (Q_{ij} =1.16, capacity 0.53). $[C_{12}mim]Cl$ also performs well in this category, making it a suitable alternative.

Figure 28 shows the results obtained for the mixtures composed of two monoterpenes: α-Pinene + β-Pinene, α-Pinene + Limonene, and p-Cymene + Limonene. The IL $[P_{6,6,6,14}][(C_8H17)_2PO_2]$ consistently emerges as the best solvent at 403.15 K. Nevertheless, as expected, the separation of these nonpolar compounds is more challenging as can be seen for the lowest Q_{ij} values, always lower than 2. For these mixtures, PEG400 does not seem to be a good alternative mainly because of the low capacity values.

Chapter 6. Conclusions and future work

Polyethylene glycols already find application as alternative green solvents in different areas, particularly in the cosmetics and pharmaceutical industries. However, the information regarding its application as mass separation agents in the fractionation and purification processes of terpenes is still very scarce. To evaluate that possibility, the infinite dilution activity coefficients of 38 organic solutes (including terpenes/terpenoids) and water in PEG400 were measured by inverse gas chromatography in different temperature ranges, within the interval of 60 °C to 120 °C.

The performance of PEG-400 to act as a MSA of several binary terpene mixtures (limonene + carvone, limonene + linalool, menthone + menthol, borneol + camphor, α-pinene + β-pinene, α-pinene + limonene, and *p*-cymene + limonene) was evaluated and compared to ionic liquids, another alternative class of low-volatile solvents. Satisfactory results were obtained only for the mixtures limonene/linalool and limonene/carvone, with solvent performance indices Q_{ij} of 1.5 and 2.4, respectively. For the remaining ones, Q_{ij} varied between 0.24 and 0.62, mainly due to the low capacities of the solutes (γ_{13}^{∞} >1). Nevertheless, PEG400 was the best option for the separation of limonene/carvone compared to the set of available ILs ([C_4mim][PF_6], [C_4mim][PF_6]/[C_4mim]Cl, [$P_{6,6,6,14}$]Cl, [$P_{6,6,6,14}$][$(C_8H_{17})_2PO_2$], [C_4mim][OAc], [C_8mim]Cl, [C_4mim]Cl/[C_{12}mim]Cl and [C_{12}mim]Cl). For the remaining mixtures envolving at least one monoterpenoid, [$P_{6,6,6,14}$]Cl had the best solvent performance index (Q_{ij} > 8). The separation of mixtures containing two hydrocarbon terpenes remains challenging, being [$P_{6,6,6,14}$][$(C_8H_{17})_2PO_2$] the best solvent with Q_{ij} varying between 1.4 and 1.6.

Regarding the experimental work, the comparison of the γ_{13}^{∞} results obtained in this work in two independent columns, for a set of organic solutes, revealed some inconsistencies (relative errors in γ_{13}^{∞} between 5 and 10%), suggesting additional studies using a third independent column.

In a broader context, future studies should also be focused on PEGs of higher molecular weight, in an attempt to increase the capacity values of terpenes and terpenoids, while maintaining the selectivities. An extension to other solutes (aromatic, sulphur and nitrogen hydrocarbon compounds) will also allow to have important insights on the use of PEGs as MSA in petrochemical processes, including separating aromatic from aliphatic hydrocarbons and the removal of impurities in fossil fuels.

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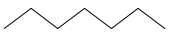
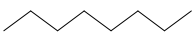
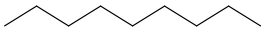
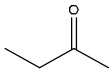
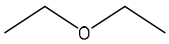
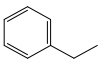
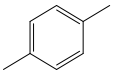
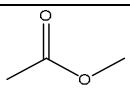
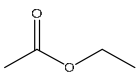
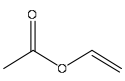
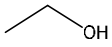
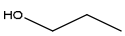
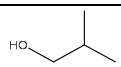
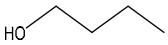
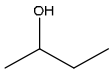
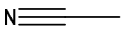
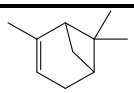
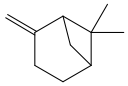
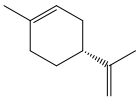
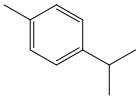
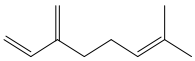
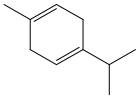
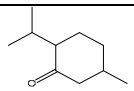
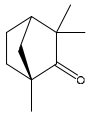
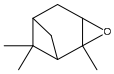
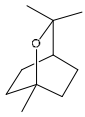
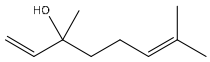
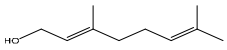
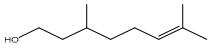
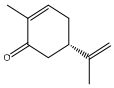
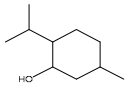
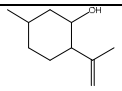
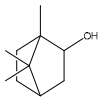
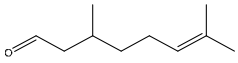
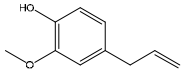
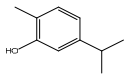
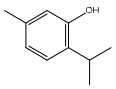
Appendix A. Chemicals

Table A1. Name, structure, source, boiling temperature, and mass fraction purity (as declared by the supplier) of the organic solutes used. Names in parentheses correspond to synonyms used in the text. Solutes stereochemistry is omitted in the main text.

Family	Name	Chemical structure	Supplier	Boiling temperature (K)	Purity (mass fraction)
Alkanes	Heptane		Aldrich	371.15[a]	≥ 0.990
	Octane		Aldrich	398.77[a]	≥ 0.990
	Nonane		Aldrich	423.91[a]	≥ 0.990
	Decane		Aldrich	447.20[a]	≥ 0.990
Cycloalkanes	Cyclohexane		Aldrich	353.90[a]	≥ 0.990
	Methylcyclohexane		Aldrich	374.00[a]	≥ 0.990
Ketones	Propanone (Acetone)		Aldrich	329.30[a]	≥ 0.999
	2-Butanone		Aldrich	353.00[a]	≥ 0.990
Ethers	Ethoxyethane (Diethyl ether)		Aldrich	307.70[a]	≥ 0.999
Cyclic Ethers	Oxolane (THF)		Aldrich	339.00[a]	≥ 0.999
	1,4-dioxane		Aldrich	374.30[a]	≥ 0.998
Aromatic Hydrocarbons	Benzene		Aldrich	353.22[a]	≥ 0.998
	Toluene		Aldrich	383.75[a]	≥ 0.998
	Ethylbenzene		Aldrich	409.35[a]	≥ 0.998
	p-xylene		Aldrich	411.5[a]	≥ 0.990
Esters	Methyl acetate		Aldrich	330.00[a]	≥ 0.998
	Vinyl acetate		Riedel-de-Häen	345.70[a]	≥ 0.990
	Ethyl acetate		Aldrich	350.20[a]	≥ 0.998
Alcohols	Methanol		Aldrich	337.80[a]	≥ 0.998
	Ethanol		Aldrich	351.50[a]	≥ 0.999
	1-propanol		Aldrich	370.30[a]	≥ 0.999
	2-propanol		Fluka	355.50[a]	≥ 0.995

Family	Name	Chemical structure	Supplier	Boiling temperature (K)	Purity (mass fraction)
	2-methyl-1-propanol (Isobutanol)		Aldrich	380.80[a]	≥ 0.998
	1-butanol		Aldrich	390.60[a]	≥ 0.995
	2-butanol		Aldrich	372.00[a]	≥ 0.997
	2-methyl-2-propanol (*tert*-butanol)		Aldrich	355.50[a]	≥ 0.999
	Acetonitrile		Fluka	355.15[a]	≥ 0.998
Terpenes	α-pinene		Aldrich	430.00[a]	≥ 0.990
	β-pinene		Aldrich	439.20[a]	≥ 0.970
	R-(+)-limonene		Aldrich	449.65[a]	≥ 0.990
	p-cymene		Aldrich	450.28[a]	≥ 0.990
	Myrcene		Aldrich	440.20[a]	≥ 0.990
	γ-terpinene		Aldrich	455.15[a]	≥ 0.970
Terpenoids	(−)-menthone		Fluka	490.79[a]	≥ 0.980
	(1*R*)-(−)-fenchone		Aldrich	466.65[b]	≥ 0.970
	α-pinene oxide		Aldrich	447.15[b]	≥ 0.990
	Eucalyptol		Aldrich	449.55[b]	≥ 0.970
	Linalool		Aldrich	471.65[b]	≥ 0.980
	Geraniol		Aldrich	502.15[b]	≈ 0.950
	DL-citronellol		Aldrich	497.65[b]	≥ 0.980
	(1*R*)-(+)-camphor		Aldrich	480.55[b]	≥ 0.980
	(*S*)-(+)-carvone		Merck	503.65[b]	≥ 0.997
	L(−)-menthol		Acros	488.55[b]	≥ 0.980

Family	Name	Chemical structure	Supplier	Boiling temperature (K)	Purity (mass fraction)
	(−)-isopulegol		SAFC	470.15[b]	≥ 0.990
	(−)-borneol		Fluka	485.15[b]	≥ 0.990
	Citronellal		Aldrich	480.15[b]	≥ 0.950
	Eugenol		Aldrich	526.35[a]	0.990
	Carvacrol		SAFC	510.15[a]	0.990
	Thymol		Sigma	505.65[a]	≥ 0.995

[a]The boiling temperature was obtained from Yaws, C.L. Thermophysical Properties of Chemicals and Hydrocarbons; 2nd ed.; Elsevier Inc., 2014.

[b]The boiling temperature was obtained from Pence, H.E.; Williams, A. Chemspider: An Online Chemical Information Resource. J. Chem. Educ. 2010, 87, 1123–1124.

Appendix B. Infinite dilution activity coefficients and capacities

Table B1. Infinite dilution activity coefficients for all solutes in the PEG-400.

Organic solutes and water	PEG400 - 1st column							PEG400 - 2nd column	
	***T*/K**	**333.15**	**343.15**	**353.15**	**363.15**	**373.15**	**383.15**	**393.15**	**333.15**	**353.15**
Heptane			13.93	12.40	11.49	10.49	9.59			
Octane		20.13	17.84	16.30	14.46	13.33	12.02		19.21	15.35
Nonane			22.98	20.13	18.13	16.59	14.75			
Decane			29.89	25.97	23.30	20.92	18.66			
Cyclohexane		5.94	5.42	5.07	4.70	4.37	4.05		5.70	4.83
Methyl acetate		1.02	1.01	1.00	1.00	1.00	0.99		0.94	0.92
Ethyl acetate			1.32	1.31	1.28	1.28	1.26			
Vinyl acetate			1.18	1.17	1.15	1.17	1.15			
THF		0.94	0.93	0.93	0.91	0.91	0.89		0.88	0.85
1,4-dioxane			0.77	0.76	0.77					
Diethyl ether			2.46	2.31	2.25					
Acetonitrile		0.62	0.63	0.65	0.65	0.66	0.67		0.56	0.59
Acetone		0.95	0.94	0.94	0.92	0.92	0.91		0.89	0.86
2-Butanone			1.14	1.13	1.11	1.11	1.09			
Methanol			0.56	0.56	0.58	0.60	0.62			
Ethanol		0.71	0.69	0.68	0.66	0.65	0.64		0.64	0.62
1-propanol			0.80	0.76	0.75	0.75	0.73			
2-propanol		0.91	0.87	0.85	0.82	0.80	0.79		0.83	0.78
Isobutanol			0.90	0.88	0.85	0.84	0.82			
1-butanol			0.94	0.91	0.89	0.87	0.84			
2-butanol				0.94	0.91	0.90	0.89			

Tert-butanol			1.16	1.13	1.12	1.10	1.08			
Water			0.55	0.50	0.47					
Terpenes/terpenoids	***T*/K**	**333.15**	**343.15**	**353.15**	**363.15**	**373.15**	**383.15**	**393.15**	**333.15**	**353.15**
α-pinene		9.61	8.78	8.23	7.64	7.20	6.82	6.42	8.87	7.62
β-pinene		7.52	6.97	6.50	6.02	5.65	5.32	4.95	6.96	5.96
Limonene			6.73	6.30	5.88	5.51	5.22	4.87		5.77
Myrcene			6.75	6.54	6.22	5.94	5.76			
γ-terpinene			4.79	4.69	4.51	4.38	4.27			
p-cymene			4.83	4.53	4.34	4.17	4.02	3.89		4.17
Eucalyptol				4.54	4.19	3.91	3.66			4.14
Low volatile terpenoids	***T*/K**	**333.15**	**343.15**	**353.15**	**363.15**	**373.15**	**383.15**	**393.15**	**333.15**	**353.15**
α-pinene oxide							1.43			
Fenchone			3.05	3.01	2.92	2.87	2.78			2.73
Menthone						3.23	3.07			
Carvone							1.49			
Citronellol						2.01	1.60			
Linalool						1.94	1.89			
Camphor						2.26	2.20			
Borneol							1.90			
Menthol							2.22			

Table B2. Capacities for all solutes in the PEG-400.

Organic solutes and water	PEG400 - 1st column							PEG400 - 2nd column	
	***T*/K**	**333.15**	**343.15**	**353.15**	**363.15**	**373.15**	**383.15**	**393.15**	**333.15**	**353.15**
Heptane			0.07	0.08	0.09	0.10	0.10			
Octane		0.05	0.06	0.06	0.07	0.08	0.08		0.05	0.07
Nonane			0.04	0.05	0.06	0.06	0.07			
Decane			0.03	0.04	0.04	0.05	0.05			
Cyclohexane		0.17	0.18	0.20	0.21	0.23	0.25		0.18	0.21
Methyl acetate		0.98	0.99	1.00	1.00	1.00	1.01		1.06	1.08
Ethyl acetate			0.76	0.76	0.78	0.78	0.79			
Vinyl acetate			0.85	0.86	0.87	0.86	0.87			
THF		1.06	1.07	1.08	1.10	1.10	1.12		1.14	1.18
1,4-dioxane			1.29	1.31	1.30					
Diethyl ether			0.41	0.43	0.44					
Acetonitrile		1.61	1.60	1.55	1.53	1.51	1.48		1.80	1.70
Acetone		1.05	1.07	1.07	1.09	1.08	1.10		1.12	1.17
2-Butanone			0.88	0.88	0.90	0.90	0.91			
Methanol			1.78	1.77	1.73	1.66	1.62			
Ethanol		1.40	1.45	1.47	1.52	1.54	1.56		1.56	1.60
1-propanol			1.25	1.31	1.33	1.34	1.37			
2-propanol		1.10	1.14	1.17	1.21	1.25	1.26		1.21	1.29
Isobutanol			1.11	1.14	1.17	1.19	1.22			
1-butanol			1.07	1.10	1.13	1.16	1.18			
2-butanol				1.06	1.09	1.11	1.12			
tert-butanol			0.86	0.88	0.90	0.91	0.92			
Water			1.83	2.00	2.11					
Terpenes/terpenoids	***T*/K**	**333.15**	**343.15**	**353.15**	**363.15**	**373.15**	**383.15**	**393.15**	**333.15**	**353.15**

α-pinene		0.10	0.11	0.12	0.13	0.14	0.15	0.16	0.11	0.13
β-pinene		0.13	0.14	0.15	0.17	0.18	0.19	0.20	0.14	0.17
Limonene			0.15	0.16	0.17	0.18	0.19	0.21		0.17
Myrcene			0.15	0.15	0.16	0.17	0.17			
γ-terpinene			0.21	0.21	0.22	0.23	0.23			
p-cymene			0.21	0.22	0.23	0.24	0.25	0.26		0.24
Eucalyptol				0.22	0.24	0.26	0.27			0.24
Low volatile terpenoids	***T*/K**	**333.15**	**343.15**	**353.15**	**363.15**	**373.15**	**383.15**	**393.15**	**333.15**	**353.15**
α-pinene oxide							0.70			
Fenchone			0.33	0.33	0.34	0.35	0.36			0.37
Menthone						0.31	0.33			
Carvone							0.67			
Citronellol						0.50	0.63			
Linalool						0.52	0.53			
Camphor						0.44	0.45			
Borneol							0.53			
Menthol							0.45			