



Ionic liquids as entrainers for terpenes fractionation and other relevant separation problems

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ABSTRACT

This work discusses the potential of two phosphonium-based ionic liquids (ILs), [P_{6,6,6,14}]Cl and [P_{6,6,6,14}][(C₈H₁₇)₂PO₂], and one methylimidazolium-based IL, [C₄mim][OAc], as entrainers in the fractionation of terpene mixtures, in the desulfurization and denitrification of fuel oils, and in the separation of aromatics from aliphatic hydrocarbons. To this aim, the activity coefficients at infinite dilution of 45 solutes were obtained by gas-chromatography in the temperature range (333.15–458.15) K. Selectivities and capacities were calculated showing that [P_{6,6,6,14}]Cl is adequate for the fractionation of (–)-menthone/L-(–)-menthol mixture, being also a suitable option for the deterpenation of citrus essential oil, and the removal of thiophene and pyridine from aliphatic hydrocarbons. To complement the experimental measurements COSMO-RS model was tested, demonstrating good potential to screen separation agents and give insights for several important separation problems, including the removal of contaminants from fuels and the isolation, fractionation and purification of terpenes mixtures.

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1. Introduction

Ionic liquids (ILs) are complex organic salts, usually presenting melting temperatures inferior to 100 °C [1,2]. Frequently composed by long-chain cations coupled with an organic or an inorganic anion, ILs exhibit unique properties including low volatility, good thermal stability and excellent solvation capability [3,4]. Among the remarkable outcomes achieved in several areas, ionic liquids have been explored as replacements of traditional organic solvents in different extraction and purification processes [3,5–8]. Thus, the knowledge of the thermodynamic properties and phase equilibria that describe the affinity between the ionic liquids and the target solutes is essential [9]. The measurement of complete phase diagrams in terms of temperature, pressure and composition is very time-consuming, while other properties such as the activity coefficients at infinite dilution can be used to screen the potential of ILs as mass separation agents, allowing to calculate parameters such as selectivity, capacity and partition coefficients, quite fundamental to design a separation process [9,10]. Within the ILs field, this technique was mostly applied to study their interaction with common organic compounds relevant in the chemical industry and refineries and, less frequently, with terpenes and their oxygenated derivatives (terpenoids). The latter are the main components of essential oils (EOs)

which are volatile, natural, and complex mixtures that can be extracted from flowers, leaves, stems, seeds, and fruits [11,12]. Due to their particular pleasant aromas and bioactivities (antioxidant, antiseptic, and anticarcinogenic), essential oils, and many of their constituents, find application in the food [13,14] cosmetic [15,16] and pharmaceutical [17–19] industries. Terpenoids are the main responsible for the aroma and antioxidant properties of EOs, while terpenes contribute little to the aroma, being easily oxidized and producing off-flavors that deteriorate the quality of the of EOs [20,21]. The removal of terpenes from the oxygenated rich part, process known as deterpenation, is crucial to improve the stability, solubility and storage requirements of commercial EOs [22,23].

The most common separation techniques employed in the deterpenation process are liquid-liquid extraction, vacuum distillation, supercritical fluid extraction, and membrane separation [20]. For industrial purposes, the liquid-liquid extraction is often desirable, since it can be carried out at mild conditions, avoiding the deterioration of the final product [14,24]. Traditionally, this technique is performed using conventional volatile organic solvents, such as methanol, hexane, acetone, ethyl acetate and petroleum ether derivatives [20]. However, alternative neoteric solvents such as hydroalcoholic solvents [25–31], deep eutectic solvents [22,32], or ionic liquids [33–38] are being studied as potential replacements, aiming at better separation performances.

In previous works from our group, methylimidazolium-based ionic liquids were investigated as separation agents in the removal of

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contaminants from aliphatic hydrocarbons [39], and in the fractionation of terpene/terpenoid mixtures [40]. This last work suggested that ILs containing the trihexyl(tetradecyl)phosphonium ($[P_{6,6,6,14}]$) cation combined with bis(2,4,4-trimethylpentyl)phosphinate $[(C_8H_{17})_2PO_2]$ or acetate [OAc] anions, were suitable for the fractionation of terpene mixtures. Besides, Lago et al. [38] proposed 1-butyl-3-methylimidazolium acetate $[C_4mim][OAc]$ for the deterpenation of citrus essential oil constituted mainly by limonene and linalool.

In this work, experimental measurements of the activity coefficients at infinite dilution and gas-liquid partition coefficients of water and 44 organic solutes (including aliphatic and aromatic hydrocarbons, esters, ethers, ketones, acetonitrile, pyridine, thiophene, alcohols, terpenes, and terpenoids) in three ionic liquids, namely trihexyl(tetradecyl)phosphonium chloride, trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate and 1-butyl-3-methylimidazolium acetate, were performed by gas chromatography in the temperature range (333.15–458.15) K. The efficiency of the ionic liquids in specific terpene/terpenoid, thiophene/alkane, and aromatic/aliphatic hydrocarbon mixtures was evaluated in terms of the selectivities and capacities, and compared with the data available in the literature for other phosphonium and imidazolium-based ionic liquids.

The use of predictive tools to estimate thermodynamic properties, such as activity coefficient at infinite dilution, is welcome in the screening of potential entrainers for separation processes, since it would reduce the amount of costly and time-consuming experimental measurements [41]. From the available options, the Conductor-like Screening Model for Real Solvents (COSMO-RS) was selected, as it has been successfully applied in the description of thermophysical data of fluids, including selectivities and capacities of relevant industrial problems [40,42–48]. Therefore, selectivities and capacities at infinite dilution predicted by the model were critically compared with the available experimental data.

2. Experimental

2.1. Materials

The chemical structure, supplier, molar mass, melting temperature and purity of the ionic liquids are presented in Table 1. Similar information for the organic solutes is presented in Table S1 of Supporting Information (SI). Before being used, all ionic liquids were dried under vacuum (at 1 Pa and 298.15 K), under continuous stirring, for at least 48 h. The organic solutes were used as received from the suppliers.

3. Methods

3.1. Chromatographic measurements

The retention times were measured using a Varian 3380 gas chromatograph (GC) equipped with a 1041 on-column injector and a thermal conductivity detector (TCD). The procedure for the column preparation and packing follows that described in previous works [39,40]. First, the stationary phase was prepared by mixing between 50% to 55% in mass of Chromosorb W/AW – DMCS (100–120 mesh) with the ionic liquid. A uniform coating of the Chromosorb with the IL was achieved by dissolving the mixture in methanol under continuous stirring, followed by the evaporation of the solvent until the original mass of the mixture was recovered (uncertainties within $\pm 1 \times 10^{-4}$ g). After, an in-house glass column (4 mm of internal diameter and 1 m of length) was filled with the stationary phase, and then placed in the GC oven. Before starting the experiments, the columns were pre-conditioned, passing the carrier gas (helium) through the column for, at least, 6 h, at 393.15 K, to ensure complete removal of possible contaminants.

The inlet pressure was registered by a Swagelok S model pressure transducer with an accuracy of 0.25% BFS, whereas the atmospheric pressure, the outlet temperature and the exit flow rate were measured

by an Agilent (model 5067-0223) Precision Gas Flow Meter. During the experiments with terpenes and terpenoids, the injector and the detector were kept at 553.15 and 573.15 K, respectively. For the other solutes, the temperatures of the injector and detector were set at 473.15 and 523.15 K, respectively. The injector and the detector were kept at the setpoint temperatures for a minimum of 30 min before starting the measurements. The temperature, pressure and flow rate uncertainties are 0.1 K, 0.05 atm and 0.6%, respectively. To achieve an infinite dilution state, the volume of injected solute varied from 0.2 to 0.4 μ L. The experiments were performed, at least, at four different temperatures in a range between 333.15–453.15 K. For a representative set of solutes (minimum 10 solutes, for each IL, including compounds from different families), the activity coefficients at infinite dilution were measured in two independent columns at three different temperatures, presenting an average coefficient of variation of 2% for $[P_{6,6,6,14}]Cl$, 2% for $[P_{6,6,6,14}][(C_8H_{17})_2PO_2]$ and 4% for $[C_4mim][OAc]$. Besides, each experiment was repeated twice to check the reproducibility of the results. The thermodynamic information (vapor pressure, density, critical properties, acentric factor, and dipole moment) of terpenes and terpenoids needed to calculate the activity and partition coefficients is available in section S1 of SI (Table S2 and Table S3), whereas these properties were obtained from DIPPR 801 database [50] for all the other organic solutes and water.

3.2. Density measurements

Density measurements of pure $[P_{6,6,6,14}]Cl$ and $[P_{6,6,6,14}][(C_8H_{17})_2PO_2]$ were performed in an automated SVM 3000 Anton Paar rotational Stabinger viscometer-densimeter in the temperature range between (278.15–373.15) K, at atmospheric pressure. The uncertainty in temperature is ± 0.02 K and the absolute uncertainty in density is $\pm 5 \times 10^{-4}$ g·cm⁻³.

3.3. Thermodynamic framework

3.3.1. Activity coefficients at infinite dilution

The experimental methodology used in this work is based on methodologies developed independently by Everett [51] and Cruickshank [52], where retention times obtained by GC measurements are used to calculate the activity coefficients at infinite dilution. Assuming that the solute injected is 1, the carrier gas is 2, and the non-volatile solvent (IL) in the stationary phase is 3, the solute activity coefficient at infinite dilution in the IL (γ_{13}^∞) is given by:

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

where n_3 is the number of moles of the ionic liquid packed in the column, R is the ideal gas constant, T is the absolute temperature of the column (regulated by the GC oven), V_N is the net retention volume of the solute, p_1^* is the saturated vapor pressure of the solute at the column temperature, B_{11} is the second virial coefficient of the pure solute, V_1^* is the molar volume of the pure solute, p_0 is the outlet column pressure, J_2^3 is the pressure correction term, B_{12} is the second virial coefficient of the solute in the carrier gas and V_1^∞ is the partial molar volume of the solute at infinite dilution. From all the variables of Eq. (1), J_2^3 and V_N require further clarification. As discussed in detail by Everett [51] and Blumberg [53], the pressure correction factor is calculated by:

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

where p_i is the inlet pressure of the column. The net retention volume, which represents the total volume the solute passes inside the column, is calculated by the following equation:

Table 1
Chemical structure, name, supplier, melting temperatures (K) and purity (mass fraction) of the studied ionic liquids.

Chemical structure cation	Anion	Chemical name and abbreviation	Supplier	Molar mass	Melting temperature (K) ^a	Mass fraction purity
	Cl ⁻	trihexyl(tetradecyl)phosphonium chloride – [P _{6,6,6,14}]Cl	Cytec	519.31	207 ± 1	≥ 0.93 ^b
		trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate – [P _{6,6,6,14}][(C ₈ H ₁₇) ₂ PO ₂]	Cytec	773.27	NA ^c	≥ 0.93 ^b
		1-butyl-3-methyl imidazolium acetate	Iolitec	198.26	210 ± 1	≥ 0.97

^a Values taken from literature.

^b Before being used, the ionic liquid was washed with distilled water several times to remove the hydrophilic contaminants and then placed into a vacuum chamber for several days to remove any additional impurities.

^c Not available.

$$V_N = \left(J_2^3 \right)^{-1} U_0 (t_r - t_g) \quad (3)$$

where t_r and t_g are the measured retention times of the solute, and a reference substance not retained by the stationary phase (usually air injected at the same time as the solute) and U_0 is the outlet volumetric flow rate (at column temperature). Once the flow rate is measured after the carrier gas leaves the detector, U_0 needs to be corrected by Eq. (4):

$$U_0 = U_f \frac{p_f}{p_0} \frac{T}{T_f} \quad (4)$$

in which U_f , p_f and T_f are, respectively, the volumetric flow, the pressure and the temperature, measured by the flowmeter. From all the variables of Eq. (1), the thermophysical properties of terpenes and terpenoids (p_1^* and V_1^*) were calculated using coefficients fitted with experimental data available in the literature. The second order virial coefficients of these solutes were estimated by the method proposed by Tsonopoulos [54], which requires the knowledge of the dipole moments, estimated using TURBOMOLE 6.1 program package applying the B-P86 density functional theory level with valence triple-zeta polarization (TZVP) basis set A complete overview of the properties used in the calculations of γ_{13}^∞ for terpenes and terpenoids is presented in Table S2 and Table S3. For all the other solutes (aliphatic and aromatic hydrocarbons, ethers, esters, ketones, alcohols, thiophene, acetonitrile, pyridine and water), the same information was compiled from DIPPR 801 [50]. For all the solutes, the mixed second virial coefficient of the solute and the carrier gas (B_{12}) were estimated by the approach proposed by Tsonopoulos [55] and discussed, in detail, by Poling et al. [56].

3.3.2. Excess partial molar properties at infinite dilution

The knowledge of γ_{13}^∞ at different temperatures allows the calculation of excess partial molar properties, namely excess enthalpy (\bar{H}_m^E),

excess Gibbs energy (\bar{G}_m^E) and excess entropy (\bar{S}_m^E). Using the linear dependence of γ_{13}^∞ with temperature (van't Hoff plot) and the chemical potential principle for an ideal solution, \bar{H}_m^E , \bar{S}_m^E and \bar{G}_m^E are obtained as follows:

$$\ln \gamma_{13}^\infty = \frac{\bar{H}_m^{E,\infty}}{R} \frac{1}{T} + \frac{\bar{S}_m^{E,\infty}}{R} \quad (5)$$

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

3.4. Gas-liquid partition coefficients

The gas-liquid partition coefficient (K_L) for a solute partitioning between the liquid phase (IL) and a carrier gas is a relevant property to describe the feasibility of a solvent in an extraction process. Similarly to the activity coefficients, the gas-liquid partition can be determined from the same GC experiments according to: [57].

$$\ln(K_L) = \frac{c_1^3}{c_1^2} = \ln \left(\frac{V_N \rho_3}{m_3} \right) - \frac{P_0 J_2^3 (2B_{12} - V_1^*)}{RT} \quad (7)$$

in which c is the molar concentration of the solute, ρ_3 is the density of the IL and m_3 is the mass of the IL in the column.

3.5. Selectivities and capacities

The performance of an entrainer in a separation problem can be easily assessed from selectivity (S_{ij}^∞) and capacity (k_j^∞) values, which are directly obtained from the activity coefficients at infinite dilution (γ_{13}^∞) using the following equations:

$$S_{ij}^\infty = \frac{\gamma_{i3}^\infty}{\gamma_{j3}^\infty} \quad (8)$$

$$k_j^\infty = \frac{1}{\gamma_{j3}^\infty} \quad (9)$$

where the subscripts i and j represent the solutes, being j the solute with the lower activity coefficient value for a given separation, and 3 refers to the ionic liquid.

3.6. COSMO-RS predictions

The COSMO-RS method combines a quantum chemistry characterization of the solute and solvent molecules with the statistical thermodynamics description of the surface interactions, being a powerful tool to predict the thermodynamic properties of liquid mixtures [58,59]. A full description of the model theoretical basis is found elsewhere [60–63]. In brief, the model requires only the structure, electronic energy and polarization charge density (σ) of each component, and from this information, COSMO-RS analyzes the interactions between the segments of each molecule in the mixture to predict the chemical potentials of the compounds. Since the activity coefficients are directly obtained from the chemical potential [63], COSMO-RS has been widely employed to estimate γ_{i3}^∞ data for water and organic solutes in liquid solvents, including ionic liquids.

The first calculation step aims to obtain the energetically optimal state of each compound, which includes its electronic energy and σ -profiles. To do so, the software TmoleX was employed [64], in which a def-TZVP basis set was applied along with the density theory level (utilizing the B–P86 functional level of theory and the COSMO solvation model). Then, the files generated by TmoleX were inputted in the software COSMOtherm [65,66], where the COSMO-RS predictions were carried out using the BP_TZVP_C30_1701.ctd parametrization. The ionic liquids were described as an equimolar and electroneutral mixture, and the activity coefficients at infinite dilution were corrected from the

hypothetically ternary mixture (solute + cation + anion) to the real binary mixture (solute + ionic liquid).

4. Results and discussion

4.1. Activity coefficients at infinite dilution

The activity coefficients at infinite dilution measured in this work at temperatures between 333.15–453.15 K are listed in Table S4 of SI. Different temperature conditions were selected for the GC measurements depending on the solute/solvent combination, as discussed in detail in Section S2 of Supporting Information.

The activity coefficients in [C₄mim][OAc] are generally higher than in [P_{6,6,6,14}Cl] or [P_{6,6,6,14}][(C₈H₁₇)₂PO₂], especially for the less polar solutes. Additionally, in [C₄mim][OAc] and [P_{6,6,6,14}Cl], γ_{i3}^∞ decreases as the temperature increases for low polar solvents such as alkanes, cycloalkanes, and terpenes. The opposite trend is observed for alcohols and terpenoids (excepting eucalyptol in [C₄mim][OAc]). In both ionic liquids, the tendencies are less pronounced for solutes presenting intermediate polarities, such as ethers, esters, and ketones. Regarding [P_{6,6,6,14}][(C₈H₁₇)₂PO₂], for most solutes the γ_{i3}^∞ do not present systematic trends with the temperature, excepting alcohols (γ_{i3}^∞ increases as T increases), or esters, ketones, 1,4-dioxane, acetonitrile, and pyridine (γ_{i3}^∞ decreases as T increases). Moreover, all the activity coefficients at infinite dilution in [P_{6,6,6,14}][(C₈H₁₇)₂PO₂] are lower than 1.

Fig. 1 explores the experimental activity coefficients of several solutes in the three ILs at the same temperature, 383.15 K. The data obtained for low volatile terpenoids in [P_{6,6,6,14}Cl] were not included in Fig. 1 as they were measured at much higher temperatures, and no data were obtained for the other two ILs.

In general, the activity coefficients increase as the number of carbons in the chemical structure increases, for a given family, and the tendency

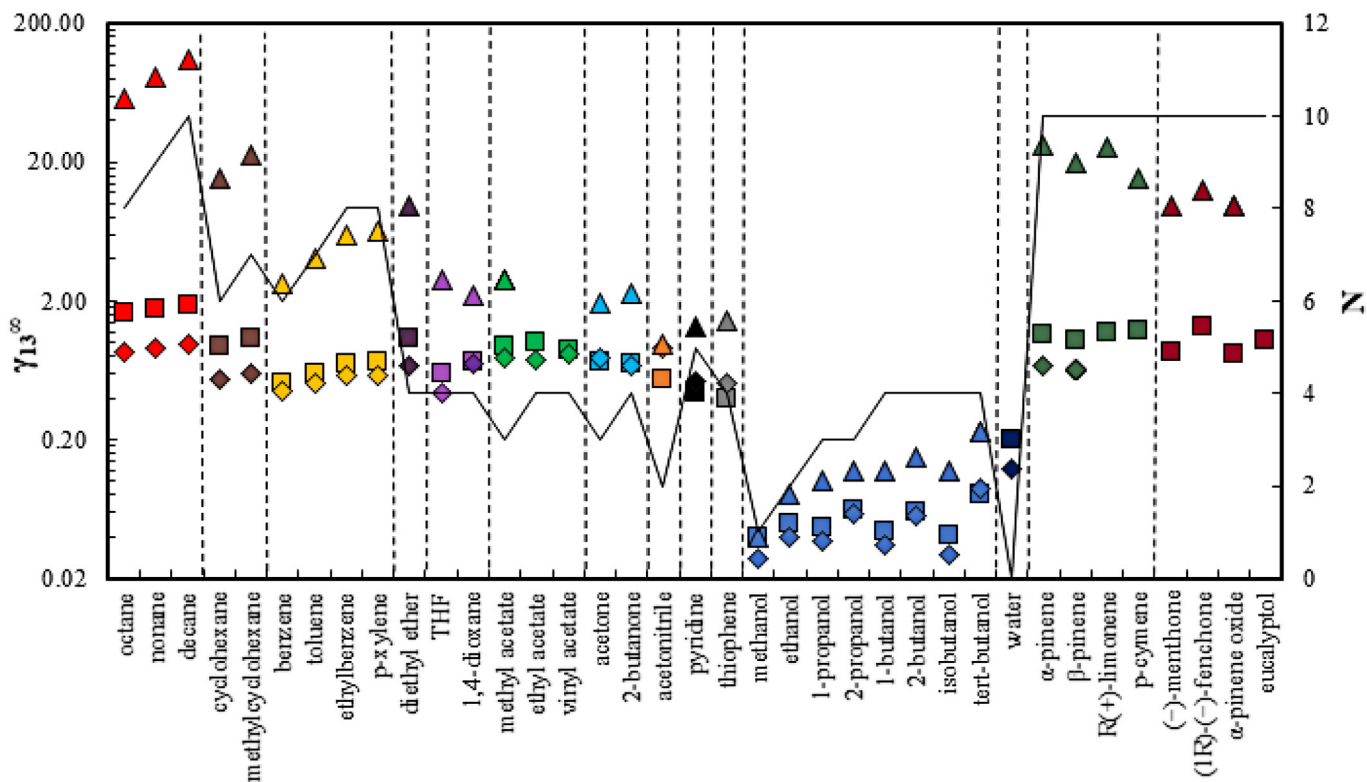


Fig. 1. Activity coefficients at infinite dilution (γ_{i3}^∞) of several organic solutes and water at 383.15 K in: \square [P_{6,6,6,14}Cl], \diamond [P_{6,6,6,14}][(C₈H₁₇)₂PO₂] and Δ [C₄mim][OAc]. The solid line represents the number of carbons (N) in the solute structure, whereas the dotted lines identify different organic families.

is more pronounced in the high polar $[C_4mim][OAc]$. For alkanes, cycloalkanes, aromatic hydrocarbons and terpenes, the activity coefficients at infinite dilution follow the order: $[C_4mim][OAc] > [P_{6,6,6,14}]Cl > [P_{6,6,6,14}][(C_8H_{17})_2PO_2]$. For $[C_4mim][OAc]$, there is always a positive deviation from ideality, indicating weak solute/IL interactions in the studied temperature range [67]. This behavior is supported by the highly polar nature of the acetate anion, with a moderate apolar hydrocarbon moiety in the imidazolium ring. The same set of solutes present γ_{i3}^{∞} values much closer to the unity in $[P_{6,6,6,14}]Cl$ or $[P_{6,6,6,14}][(C_8H_{17})_2PO_2]$. For both, the long carbon chains present in the cation $[P_{6,6,6,14}]^+$ are extensive non-polar domains increasing the magnitude of the van der Waals interactions between the solutes and the ionic liquid leading, in some cases, to behaviors close to ideal. A similar outcome is observed comparing the anion effect in the activity coefficients of hydrocarbons in $[P_{6,6,6,14}]Cl$ or $[P_{6,6,6,14}][(C_8H_{17})_2PO_2]$, since dispersion forces in bis(2,4,4-trimethylpentyl)phosphinate ($[(C_8H_{17})_2PO_2]^-$) are stronger than with the chloride anion.

For alcohols, the general trend follows the same order observed for the hydrocarbons, but it presents γ_{i3}^{∞} values much lower than aliphatic or aromatic hydrocarbons. In fact, all alcohols present activity coefficients considerably lower than 1, indicating very strong interactions between the solutes and the ionic liquids, which can be attributed mainly to hydrogen bonding.

To the best of our knowledge, experimental γ_{i3}^{∞} values of various solutes in the studied ILs are reported for the first time, including terpenes, terpenoids, esters, ketones, acetonitrile, pyridine, thiophene, and water. For some alkanes, aromatics and alcohols, the γ_{i3}^{∞} obtained in this work were compared with the scarce data available in the literature. Globally, a very satisfactory agreement between our data and those previously published was found, giving excellent indications about the consistency of the data measured in this work. This analysis is presented in Fig. S1 and discussed in more detail in Section S2 of SI.

4.2. Gas-liquid partition coefficients

The ILs density is needed to calculate the partition coefficients, and the data obtained in this work are also discussed in detail in Section S2 of SI, where Fig. S2 and Table S5 show an extensive comparison to the literature data. For $[C_4mim][OAc]$, the data reported by Almeida et al. [68] were used, while for $[P_{6,6,6,14}]Cl$ and $[P_{6,6,6,14}][(C_8H_{17})_2PO_2]$ the data measured in this work, and presented in Table S6 of SI, were employed.

The gas-liquid partition coefficients obtained in this work are presented in Table S7 of the Supporting Information. This property provides insights on the suitability of the ionic liquid for industrial separation processes, e.g. a liquid-liquid extraction followed by evaporation of the solutes at low pressures. Regarding the essential oils, K_L is a useful tool to evaluate the use of ionic liquids in the fractionation of the terpenes mixtures, followed by the recovery and purification of the final product [40].

For all the studied solutes, a temperature increment leads to lower K_L values, and consequently, lower concentrations in the liquid phase. To better understand the relationship of this parameter with the structure and functionality of the solutes, Fig. 2 shows the K_L values measured at 383.15 K.

The gas-liquid partition coefficients increase with the alkyl-chain in aromatic or aliphatic hydrocarbons, ketones, or esters. In fact, low temperatures and large alkyl chains in the solutes contribute to enhance the solute-IL interactions, especially for the less polar $[P_{6,6,6,14}]Cl$ and $[P_{6,6,6,14}][(C_8H_{17})_2PO_2]$. Fig. 2 also informs that partition coefficients of aliphatic hydrocarbons, terpenes, and thiophene in $[C_4mim][OAc]$ are considerably lower than in the other two ionic liquids. This behavior is due to the poor affinity between the highly polar $[C_4mim][OAc]$ and low polar solutes. Nevertheless, $[C_4mim][OAc]$ shows the highest K_L values for alcohols, most probably due to the formation of hydrogen

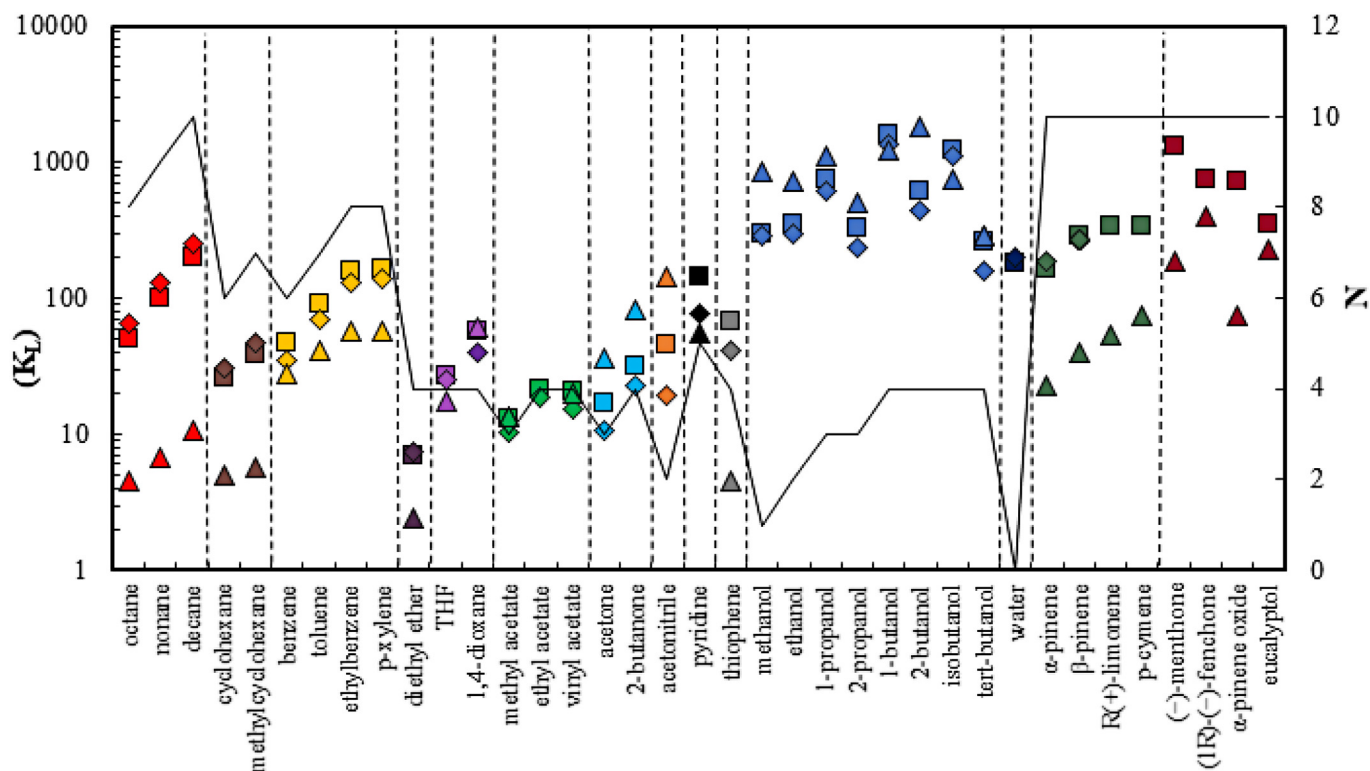


Fig. 2. Gas-liquid partition coefficients (K_L) of several organic solutes and water at 383.15 K in \square $[P_{6,6,6,14}]Cl$, \diamond $[P_{6,6,6,14}][(C_8H_{17})_2PO_2]$ and Δ $[C_4mim][OAc]$.

bonds between the anion $[\text{OAc}]^-$ and the hydroxyl groups from the alcohols, which increases the solute-solvent affinity in the liquid phase. Considering the ILs $[\text{P}_{6,6,6,14}]\text{Cl}$ and $[\text{P}_{6,6,6,14}][(\text{C}_8\text{H}_{17})_2\text{PO}_2]$, the gas-liquid partition coefficients of each solute in the ionic liquids presents the same order of magnitude. By analyzing Table S7 of SI, it is possible to see that some terpenoids, such as geraniol, DL-citronellol, (–)-borneol and L-(–)-menthol, present high K_L at higher temperatures, although K_L tends to decrease as the temperature increases. From all the calculated values, the lowest partition coefficient was obtained for diethyl ether in $[\text{C}_4\text{mim}][\text{OAc}]$ at 383.15 K ($K_L=2.447$), whereas the highest value was found for geraniol in $[\text{P}_{6,6,6,14}]\text{Cl}$ at 433.15 K ($K_L=7114$). The differences between the partition coefficient values in $[\text{P}_{6,6,6,14}]\text{Cl}$ (moderate K_L values were obtained for terpenes and higher K_L were found for low volatile terpenoids) suggest this ionic liquid to be a suitable agent for the deterpenation of commercial EOs through distillation, since the volatilization of the hydrocarbon terpenes is facilitated in presence of that IL.

4.3. Infinite dilution thermodynamic functions

Partial molar functions at infinite dilution, namely excess Gibbs energy ($\bar{G}_m^{E,\infty}$), enthalpy ($\bar{H}_m^{E,\infty}$), and entropy ($\bar{S}_m^{E,\infty}$) were calculated at 383.15 K and 433.15 K for several solutes in the studied ionic liquids. The results are presented in Fig. S3 and in Table S8 of SI. In the three ionic liquids, similar patterns were observed regarding the partial molar thermodynamic functions for alcohols and most of the terpenoids. For these solutes, the $\bar{H}_m^{E,\infty}$ and the $\bar{S}_m^{E,\infty}$ values are generally negative, suggesting a dominant enthalpic effect in the interactions between the solutes and the IL. Besides, the negative $\ln(\gamma_{13}^\infty)$ values obtained for these solutes indicates that the affinity between the solute and the IL is stronger than the solute-solute or IL-IL interactions, which was qualitatively noticed from the long retention times registered during the GC experiments.

In the case of apolar solutes, such as alkanes, cycloalkanes, aromatic hydrocarbons, and terpenes, in $[\text{P}_{6,6,6,14}]\text{Cl}$ and $[\text{P}_{6,6,6,14}][(\text{C}_8\text{H}_{17})_2\text{PO}_2]$, $\bar{H}_m^{E,\infty}$ and $\bar{S}_m^{E,\infty}$ are in general positive, and present much lower absolute values (smaller than $3 \text{ kJ}\cdot\text{mol}^{-1}$) than the highly polar solutes (alcohols, water and terpenoids). For most of these cases, $\bar{G}_m^{E,\infty}$ is close to zero, indicating that the enthalpic and entropic effects cancel each other. For the less polar solutes in $[\text{C}_4\text{mim}][\text{OAc}]$, $\bar{H}_m^{E,\infty}$ is generally positive, while $\bar{S}_m^{E,\infty}$ is mostly negative, resulting in very positive $\bar{G}_m^{E,\infty}$ values.

A more detailed discussion about the solute-IL affinity obtained from these thermodynamic functions is presented in Section 2 of Supporting Information.

4.4. Selectivities and capacities

Besides the separation problems discussed in the following sections, the separation of benzene from aliphatic hydrocarbons is addressed in Section S2 of SI, where the selectivities and capacities obtained in this work (at 333.15 K) are critically compared with the data available in literature [69,70] and presented in Table S9. In summary, the results show that the experimental data obtained here are in excellent agreement with the data found in literature, and $[\text{C}_4\text{mim}][\text{OAc}]$ presents favorable selectivities, although poor capacities, for the removal of benzene from octane and cyclohexane.

4.4.1. Terpene mixtures

A suitable entrainer in liquid-liquid extraction should promote high selectivities (S_{ij}^∞), and capacities (k_j^∞), to provide an efficient separation of the components without the formation of immiscible mixtures [71,72]. Since one of the main perspectives of this work is to explore the performance of the ionic liquids in the fractionation of terpene

mixtures, experimental and predicted selectivities and capacities (by COSMO-RS), obtained at 403.15 K, are presented in Fig. 3 (and Tables S10-S15 of SI). In some cases, the experimental selectivities and capacities were extrapolated to 403.15 K using experimental data obtained at 433.15–458.15 K.

The three ionic liquids showed poor experimental and predicted selectivities (< 2) for the terpene/terpene separations such as the α -pinene/ β -pinene, β -pinene/R(+)-limonene and p-cymene/R(+)-limonene mixtures. In particular, the fractionation of α -pinene/ β -pinene mixture is commercially attractive due to the high concentration of these compounds in several essential oils from *Pinus* species [73,74]. However, the similarities between the chemical structures and the physical properties of these compounds are handicaps in the fractionation of this mixture through solvent extraction processes or distillation. Regarding the COSMO-RS predictions, the model provides S_{ij}^∞ and k_j^∞ values which are in very good agreement with the experimental data for most of the studied terpene/terpene separations. Nevertheless, the model shows that the ionic liquids present a higher potential for the fractionation of some terpene/terpenoid mixtures, which is validated by the experimental results.

For $[\text{C}_4\text{mim}][\text{OAc}]$, encouraging experimental selectivities were found for terpene/linalool mixtures, being the highest found for R(+)-limonene/linalool ($S_{ij}^\infty = 30.29$). This particular mixture represents the majority of the components present in Citrus essential oils profiles [20,22,75], and the removal of R(+)-limonene improves the oil stability [21]. The high selectivity value found for the R(+)-limonene/linalool mixture along with the reasonable capacity of linalool (1.26) at 403.15 K suggest that $[\text{C}_4\text{mim}][\text{OAc}]$ is a potential option in the deterpenation of citrus essential oils, in accordance with the study of Lago et al. [38]. The authors obtained liquid-liquid equilibrium data for R(+)-limonene/linalool/ $[\text{C}_4\text{mim}][\text{OAc}]$ ternary systems, concluding that the ionic liquid exhibits a good performance in the deterpenation of citrus essential oil due to the strong affinity of the acetate anion with the hydroxyl group present in linalool.

In the case of $[\text{P}_{6,6,6,14}]\text{Cl}$ many other separations can be discussed, since the experimental measurements were conducted for a larger set of terpenoids. Despite the low selectivities and capacities obtained for mixtures of terpenes, promising values were found for some terpene/terpenoid and terpenoid/terpenoid combinations. The experimental selectivity and capacity (at 403.15 K) obtained for R(+)-limonene/linalool were $S_{ij}^\infty = 10.20$ and $k_j^\infty = 9.01$, respectively, suggesting $[\text{P}_{6,6,6,14}]\text{Cl}$ to be also an appropriate solvent in the deterpenation of citrus oils. In addition, promising selectivities and capacities ($S_{ij}^\infty = 10.16$ and $k_j^\infty = 11.72$) were observed for the fractionation of (–)-menthone/L-(–)-menthol mixture, which can be found in high concentrations in peppermint essential oils [76–78]. Another potential separation problem is the fractionation of the (–)-borneol/camphor mixture, widely present in the essential oils from flowers of the *Asteraceae* [79,80] and *Lamiaceae* [81–83] families. Again, a high selectivity ($S_{ij}^\infty = 9.03$) and capacity of (–)-borneol ($k_j^\infty = 14.15$) were obtained with $[\text{P}_{6,6,6,14}]\text{Cl}$. For this ionic liquid, the COSMO-RS predictions showed, in general, lower selectivities and capacities. In particular, for the binaries mentioned above for the R(+)-limonene/linalool ($S_{ij}^\infty = 3.59$ and $k_j^\infty = 4.29$), the menthone/L-(–)-menthol ($S_{ij}^\infty = 2.44$ and $k_j^\infty = 3.80$), and the (–)-borneol/camphor ($S_{ij}^\infty = 2.33$ and $k_j^\infty = 3.81$) mixtures, but still higher than the values predicted for terpene/terpene mixtures. Although COSMO-RS is able to correctly predict the selectivity ranks and capacity (terpene/low volatile terpenoid > terpene/terpenoid > terpene/terpene), the real potential of the $[\text{P}_{6,6,6,14}]\text{Cl}$ for the fractionation of mixtures containing a terpenoid with a hydroxyl group combined with terpene or terpenoids without such a group were obtained from the experimental results.

Good capacities are obtained for most of the solutes in $[\text{P}_{6,6,6,14}][(\text{C}_8\text{H}_{17})_2\text{PO}_2]$, but the selectivities are low for most of the binary mixtures studied, being 8.18 the highest experimental value achieved ((1R)-(–)-fenchone/linalool) and 4.54 the best predicted value

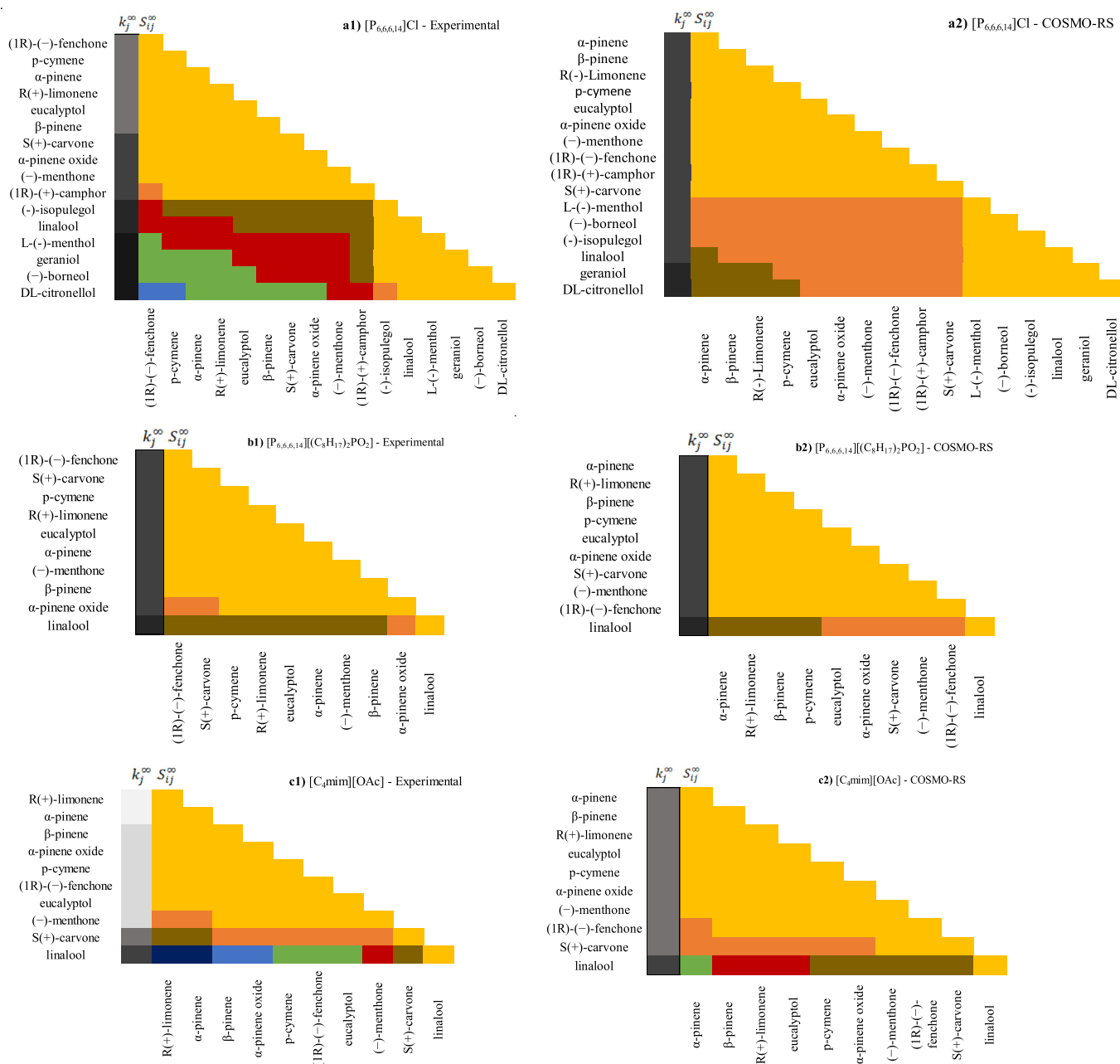


Fig. 3. Experimental and predicted S_{ij}^{∞} and k_j^{∞} between terpenes and terpenoids at 403.15 K for: a) [P_{6,6,6,14}]Cl; b) [P_{6,6,6,14}][(C₈H₁₇)₂PO₂]; c) [C₄mim][OAc]. Color code for selectivities: auburn [1–2]; salmon [2–4]; brown [4–10]; red [10–15]; green [15–20]; blue [20–25] and navy >25; and capacities: off-white: <0.05; light gray [0.05–0.1]; medium gray [0.1–1]; dark gray [1–5]; charcoal [5–10]; and black >10.

(α -pinene/linalool). In fact, from the analyzed terpenic binary mixtures, [P_{6,6,6,14}][(C₈H₁₇)₂PO₂] only presents some separation potential for those containing linalool, which was observed in both experimental and predicted selectivities and capacities. In comparison with [P_{6,6,6,14}]Cl and [C₄mim][OAc], the presence of long alkyl-chains in [P_{6,6,6,14}]⁺ and in [(C₈H₁₇)₂PO₂]⁻ increases the affinity of low polar solutes and [the ionic liquid, resulting in lower selectivities. In a previous study from our group [40], selectivities and capacities for terpene mixtures were calculated (at 408.15 K), considering four methylimidazolium-based ILs: 1-butyl-3-methylimidazolium chloride ([C₄mim]Cl), 1-butyl-3-methylimidazolium methanesulfonate ([C₄mim][CH₃SO₃]), 1-butyl-3-methylimidazolium dimethyl phosphate ([C₄mim][(CH₃)₂PO₄]) and 1-butyl-3-methylimidazolium trifluoromethanesulfonate

([C₄mim][CF₃SO₃]). In general, the best selectivities and capacities were found for mixtures containing eugenol, thymol, and carvacrol, which were not studied in this work. Moreover, good selectivities and capacities were achieved for terpenic mixtures containing (–)-borneol, (–)-isopulegol, and (1R)-(+)-camphor, which was also observed in this work for [P_{6,6,6,14}]Cl. Similarly to the selectivities obtained in this work, for the α -pinene/ β -pinene mixture, the authors also reported poor selectivity using any of the ILs investigated. As discussed before, the fractionation of the α -pinene/ β -pinene mixture is challenging, and the use of ionic liquids or another type of entrainers requires further research. In the case of the (–)-menthone/L-(–)-menthol mixture, the most promising selectivities were reported for [C₄mim]Cl ($S_{ij}^{\infty} = 8.77$), which is close to the value extrapolated at 408.15 K using the

Table 2

S_{ij}^{∞} and k_j^{∞} of octane/thiophene and octane/pyridine separations in imidazolium and phosphonium-based ionic liquids at 333.15 K.

Ionic liquid	Selectivities (S_{ij}^{∞})/capacities (k_j^{∞})		Reference
	Octane/thiophene	Octane/pyridine	
<i>Phosphonium-based ionic liquids</i>			
[P _{1,4,4,4}][TOS]	19.20/1.21 ^a	–	[88]
[P _{2,4,4,4}][DEP]	8.23/1.71 ^a	8.81/1.84 ^a	[89]
[P _{1,4,6,6,6}][NTf ₂]	3.63/2.57 ^a	3.81/2.70 ^a	[90]
[P _{6,6,6,14}][Br]	–	3.89/2.09	[91]
[P _{6,6,6,14}][Cl]	4.93/2.81	4.17/2.38	This work ^c
	3.46/2.22	4.93/2.81	This work ^d
[P _{6,6,6,14}][(C ₈ H ₁₇) ₂ PO ₂]	1.62/1.90	1.44/1.70	This work ^c
	1.84/2.14	1.29/1.50	This work ^d
<i>1-butyl-3-methylimidazolium-based ionic liquids</i>			
[C ₄ mim][Cl]	243.46/0.58 ^b	347.97/0.82 ^b	[39]
[C ₄ mim][BF ₄]	190.03/0.67 ^b	312.60/1.06 ^b	[92]
[C ₄ mim][SCN]	180.34/0.78 ^a	–	[93]
[C ₄ mim][CHSO ₃]	129.81/0.69 ^b	16.37/0.09 ^b	[39]
[C ₄ mim][DCA]	109.23/0.87 ^b	137.43/1.09 ^b	[94]
[C ₄ mim][TCM]	87.59/1.49 ^a	96.13/1.64 ^a	[95]
[C ₄ mim][PF ₆]	66.37/0.68	120.46/1.23	[96]
[C ₄ mim][TOS]	60.38/0.91 ^a	–	[97]
[C ₄ mim][(CH ₃) ₂ PO ₄]	51.81/0.98 ^b	51.07/0.97 ^b	[39]
[C ₄ mim][CF ₃ SO ₃]	50.60/0.86 ^a	–	[98]
[C ₄ mim][BETI]	17.49/1.68 ^a	32.5/3.13 ^a	[99]
[C ₄ mim][(C ₈ H ₁₇ OSO ₃)]	10.10/1.28 ^a	–	[100]
[C ₄ mim][n-C ₁₈ H ₃₅ OO]	2.00/1.25	–	[101]
[C ₄ mim][n-C ₁₆ H ₃₁ OO]	1.78/1.11	–	[101]
[C ₄ mim][OAc]	69.54/0.81	67.89/0.78	This work ^c
	18/72/1.11	17.67/1.05	This work ^d

^a Interpolated using the data reported by the authors.

^b Extrapolated using the data reported by the authors.

^c Experimental values.

^d Predicted using COSMO-RS.

experimental data obtained here for [P_{6,6,6,14}][Cl] ($S_{ij}^{\infty} = 9.88$). However, a major difference is observed for the capacities of L-(–)-menthol: $k_j^{\infty} = 0.10$ for [C₄mim][Cl] and $k_j^{\infty} = 10.84$ for [P_{6,6,6,14}][Cl], indicating that this is a more suitable option as separation agent for the fractionation of peppermint essential oils.

4.4.2. Desulfurization and denitrification of fossil fuels

The emission of sulfur- and nitrogen-compounds from the burning of fossil fuels is a known cause of acid rain, and respiratory diseases [84,85]. Environmental regulations aiming at the reduction of the emissions [5,84], and new limits for the sulfur and nitrogen containing compounds in the fuels require alternatives to the traditional separation techniques. The use of ionic liquids is promising, since they are usually capable of solubilizing the nitrogen and sulfur-based components, while presenting low affinity for the aliphatic hydrocarbons of the fuels [86,87]. The potentialities of [P_{6,6,6,14}][Cl], [P_{6,6,6,14}][(C₈H₁₇)₂PO₂] and [C₄mim][OAc] in the desulfurization and denitrification of fuels are, therefore, here evaluated in terms of the selectivities and capacities for the octane/thiophene and octane/pyridine separations. Table 2 compares the information obtained in this work (at 333.15 K), with the data reported in literature for other phosphonium-based and 1-butyl-3-methylimidazolium-based ionic liquids.

The selectivities reported for 1-butyl-3-methylimidazolium-based ionic liquids are usually higher for both octane/thiophene and octane/pyridine separations than the selectivities of the phosphonium-based ILs, while the capacities generally tend to be the opposite. From all the ionic liquids presented in Table 2, the most appropriate options to perform both desulfurization and denitrification of fossil fuels are [C₄mim][Cl] and [C₄mim][BF₄], since both ILs present considerably high selectivities and acceptable capacity values. In the case of the ILs studied in

this work, [C₄mim][OAc] presents the highest selectivity, being also an adequate option for the removal of sulfur-based and nitrogen-based contaminants from fuel oils.

As discussed before, the capacity plays an important role in the solvent selection, and very low capacities must be rejected. However, low selectivities could imply poor separation efficiency, making the separation difficult or not viable. In general, the ionic liquids composed by phosphonium cations present satisfactory capacities (always higher than 1), but their low selectivities for the octane/thiophene and octane/pyridine mixtures limits the use of these ILs. A clear exception is [P_{1,4,4,4}][TOS], which presents a high selectivity and reasonable capacity for the removal of thiophene from aliphatic hydrocarbons. A possibility to be explored in the future is the use of mixtures of two or more ionic liquids as the GC stationary phase, as previously reported by Shida and co-authors [102]. The presence of two phosphonium-based ILs with different selectivities and capacities (e.g., the equimolar mixture of [P_{1,4,4,4}][TOS] and [P_{6,6,6,14}][Cl]) could increase capacity values, while retaining the good selectivities for the desulfurization of fossil fuels.

The predictions of COSMO-RS are in excellent agreement with the experimental values for the phosphonium-based ILs, whereas more significant deviations are observed for the highly polar [C₄mim][OAc]. In fact, it is expected that COSMO-RS predictions present larger errors for systems containing highly polar compounds, since the model is unable to take into account some specific hydrogen bonds [59,103]. Nevertheless, the COSMO-RS model provided *a priori* qualitative estimations of S_{ij}^{∞} and k_j^{∞} values for both octane/thiophene and octane/pyridine mixtures, suggesting that the model is a reliable tool to be used in the screening of potential entrainers for these separation problems.

5. Conclusions

In this work, the potential of [P_{6,6,6,14}][Cl], [P_{6,6,6,14}][(C₈H₁₇)₂PO₂] and [C₄mim][OAc] as separation agents for relevant industrial separations problems was investigated through experimental and modeling approaches. The activity coefficients at infinite dilution and the gas-liquid partition coefficients were experimentally obtained for water, common organic solvents and terpenes in the three ionic liquids by gas-chromatography, in the temperature range 333.15–453.15 K. The differences between the gas-liquid partition coefficients for terpenes and low volatile terpenoids indicate that [P_{6,6,6,14}][Cl] holds a good potential as agent for the purification of terpenic mixtures.

The excess partial molar properties ($\bar{H}_m^{E,\infty}$, $\bar{S}_m^{E,\infty}$ and $\bar{G}_m^{E,\infty}$) were derived from the activity coefficients. The results show that the strong polar solutes present high affinity with the ILs dominated by enthalpic contributions, whereas the interactions between the less polar solutes and the ionic liquids are weaker, especially for [C₄mim][OAc].

Selectivities and capacities were calculated from the experimental values to evaluate the efficiency of the ILs as entrainers in the separation of aromatics from aliphatic compounds, the fractionation of essential oils, and the desulfurization and denitrification of fossil fuels. The experimental results were also compared with the estimated S_{ij}^{∞} and k_j^{∞} from the predictive COSMO-RS model. Both experimental and modeling approaches showed that [C₄mim][OAc] is an interesting option for removing sulfur and nitrogen impurities of fossil fuels. This IL also presents relevant selectivity values for the removal of benzene from alkanes and cycloalkanes, and it is an excellent candidate for the deterpenation of orange essential oils. The three ILs studied in this work are suitable separation agents, in terms of selectivities and capacities, for the fractionation of limonene/linalool mixtures, which corresponds to the major fraction of several citrus essential oils.

The S_{ij}^{∞} and k_j^{∞} values calculated for terpenic mixtures in presence of [P_{6,6,6,14}][Cl] also reveal an excellent potential for the fractionation of other major components of EOs, namely menthone/menthol, and borneol/camphor. However, the ILs studied in this work present poor

selectivity and capacity for all terpene/terpene mixtures, including the complex α -pinene/ β -pinene separation problem. In general, the trends obtained from the experimental selectivities and capacities for the fractionation of the terpenic mixtures were also observed in the predicted results, even though COSMO-RS usually underestimated them, presenting bigger deviations for mixtures containing hydrogen-bond donor terpenoids with an IL with a hydrogen-bond acceptor character. Therefore, the COSMO-RS holds a good potential to screen separation agents for the fractionation of mixtures containing terpenes, including several essential oils, as well as the separation of impurities from fossil fuels.

CRediT authorship contribution statement

Sérgio M. Vilas-Boas: Investigation, Writing - original draft, Data curation, Software. **Gabriel Teixeira:** Investigation. **Sabrina Rosini:** Investigation. **Mónia A.R. Martins:** Investigation, Data curation. **Priscilla S. Gaschi:** Writing - review & editing. **João A.P. Coutinho:** Supervision, Writing - review & editing. **Olga Ferreira:** Supervision, Project administration, Writing - review & editing. **Simão P. Pinho:** Supervision, Project administration, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary Data

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