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# Evaluation of Ionic Liquids for the Sustainable Fractionation of Essential Oils

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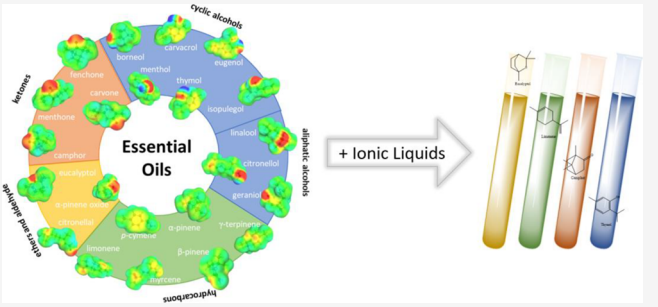
**ABSTRACT:** Fractionation of terpenes from natural complex matrices is economically attractive due to the wide use of these compounds in the cosmetic, food, and pharmaceutical industries. In this study, the potentialities of ionic liquids (ILs), and their mixtures, as separation agents in the fractionation of essential oils, were assessed through experimental and modeling approaches. Inverse gas chromatography was used to investigate solute−solvent interactions, and the COSMO-RS predictive model was applied to describe the experimental data and to search for other potential ILs by selecting the appropriate cation−anion combination. Both the experimental and predicted approaches demonstrate that chloride-based ILs are very good options for fractionating essential oils containing hydrogen-bond donor monoterpenoids. In particular, the experimental and COSMO-RS screenings suggest that $[P_{6,6,6,14}]Cl$ gives the best performance for the separation of the main components present in citrus, mentha, and basil essential oils. The results gathered herein allow a deep understanding of terpene-IL interactions, and support the prediction of the ILs performance in the extraction and separation of natural products, optimizing resources and promoting sustainability.




## INTRODUCTION

Terpenes and their oxygenated derivatives, terpenoids, are a class of organic compounds omnipresent in nature, particularly in higher plants.[1] Among their most relevant subclasses are monoterpenes and monoterpenoids, ten-carbon-containing substances widely found in essential oils (EOs).[2,3] Apart from their pleasant aromas, these compounds exhibit several interesting bioactivities, such as antioxidant, anti-inflammatory, antimicrobial, and analgesic,[1] being very attractive for cosmetic, pharmaceutical, and food industries.[4,5]

Due to their abundance in nature, a convenient method to obtain value-added terpenes is their extraction and purification from natural complex matrices, such as EOs.[2,6] In this field, the most employed industrial processes are solvent extraction, distillation, chromatography,[3,6] and, less commonly, membrane separation and supercritical extraction.[2] A combination of these techniques might be also advantageous; for instance, starting with solvent extraction of the volatile fractions, followed by distillation processes to separate the lower and heavier portions, and finally a chromatographic technique for the isolation of the target compounds.[6] From another perspective, the removal of the sparingly soluble hydrocarbon-based fraction from the oxygenated terpene fraction in commercial EOs, a process known as deterpenation, is of utmost importance to improve the quality of the final product.[2,7]

Ionic liquids are promising candidates to replace traditional organic solvents as separation agents in the extraction, isolation, and purification of biomolecules, having been extensively studied in those fields in the last few years.[8] Besides their appealing properties, such as low volatility, great solvation ability, and excellent thermal stability,[9,10] these solvents can be tailored by combining different cations and anions, to reach specific physicochemical properties, expanding their range of applications.[11,12] Within the scope of terpene separation and purification, the potentialities of imidazolium ILs to produce terpeneless citrus EOs have been extensively investigated by Soto and co-authors.[13−16] Besides, imidazolium and phosphonium-based ILs showed the potential to fractionate several monoterpene/monoterpenoid mixtures present in different EOs.[17,18] Recently, *deep* eutectic solvents (DES) have also been pointed out as potential alternatives to fractionate citrus EOs.[19−22]

When designing extraction and distillation processes, selecting a suitable solvent or entrainer plays a key role.

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Nonetheless, that selection is a time and resource-consuming task, and strategies for systematic solvent pre-selection are valuable in reducing the labor intensity of this task.[23,24] In this context, the knowledge of the activity coefficients at infinite dilution of a solute in a given solvent arises as a valuable tool since this property provides important information on the solute−solvent interactions, while it can be obtained efficiently through chromatographic methods.[24] The activity coefficients can be used to determine the separation factors of relevance for measuring the potential of a solvent to act as a separating agent in a specific separation.

In our previous studies,[17,18] we have shown the potential of inverse gas chromatography as a pre-selection technique to quantitatively measure the affinity between solutes and solvents. In the present study, the interactions between terpene mixtures, representative of EOs, and 1-octyl-3-methylimidazolium chloride ([$C_8$mim]Cl), 1-dodecyl-3-methylimidazolium chloride ([$C_{12}$mim]Cl), and the ILs mixture composed by 1-butyl-3-methylimidazolium chloride ([$C_4$mim]Cl) and [$C_{12}$mim]Cl in the equimolar proportion, were investigated through the measurement of the activity coefficient at infinite dilution. ILs were chosen aiming to infer about the increase of the cation alkyl chain length on the solvation ability. Additionally, the ability of the predictive COnductor-like Screening Model for Real Solvents (COSMO-RS) to describe the experimental separation factors for the Cl-based ILs was tested, and predictions were extended to imidazolium-based ILs with other anions, including tetrafluoroborate ($[BF_4]^-$), ethyl sulfate ($[C_2H_5SO_4]^-$), butyl sulfate ($[C_4H_9SO_4]^-$), and octyl sulfate ($[C_8H_{17}SO_4]^-$). The model has been successfully applied to screen promising solvents to isolate terpenes from natural matrices.[19,20,22,25] The knowledge gathered in this study aims to guide the design of ILs for a more sustainable fractionation of EOs.

## EXPERIMENTAL SECTION

**Chemicals.** The terpenes used in this study are presented in Table S1 of Supplementary Material (SM), while ILs are described in Table S2. Before being used, ILs were dried under vacuum and continuous stirring at 1 Pa and 298.2 K, for at least 48 h. The terpenes stereochemistry is omitted in the manuscript text.

**Chromatographic Procedure.** To achieve a uniform coating of the stationary phase, the solid support (Chromosorb W/AW—DMCS, 100−120 mesh) and the ILs were dissolved in methanol under continuous stirring, followed by the evaporation of the solvent using a vacuum-assisted rotary evaporator. The mixture was dried until the difference between the original and final masses was lower than 0.1 mg. Afterward, the stationary phase was packed in an in-house glass column (1 m in length and 0.4 cm of internal diameter) using a vacuum pump. The [$C_4$mim]Cl:[$C_{12}$mim]Cl equimolar mixture (0.503, 0.497 mole ratio) was prepared in a Mettler Toledo scale (model XP205, readability ±0.01 mg). The IL mass fractions in the stationary phases were 0.5272 for [$C_8$mim]Cl, 0.4640 for [$C_{12}$mim]Cl, and 0.4650 for [$C_4$mim]Cl/[$C_{12}$mim]Cl equimolar mixture. Relevant thermodynamic properties were calculated from the experimental retention times obtained by inverse-gas chromatography, following the procedure described elsewhere[18,26,27] and detailed in Section SM.2. The solute's thermophysical properties and constants, required for the calculations, are available in Tables S3 and S4.

**COSMO-RS Predictions.** The activity coefficients at infinite dilution were computed using the COSMOtherm 2021 software[28,29] with the BP_TZVP_21.ctd level of parametrization. The ILs were considered as equimolar and electroneutral mixtures of cations and anions, and the calculations were performed for hypothetically ternary (solute + cation + anion) mixtures. Then, the obtained activity coefficients at infinite dilution in the hypothetically ternary mixture were corrected to the real binary mixture (solute + IL) by applying a scale factor of 0.5 to the predicted values, following the methodology presented by Klamt and co-authors.[30,31] The input COSMO files for most cations and anions were collected from the COSMOtherm database. For $[C_{12}mim]^+$, $[C_8H_{17}SO_4]^-$, and the studied monoterpenes, the COSMO files were obtained using the COSMOconfX 2021 software combined with the TmoleX (version 4.5) package,[32] applying the BP-TZVPD-FINE-COSMO+GAS_18 template. All the generated conformers were considered in the COSMOtherm calculations. For the IL mixture, the cation was treated as an equimolar mixture of $[C_4mim]^+$ and $[C_{12}mim]^+$.

**Thermodynamic Background. Activity Coefficients at Infinite Dilution.** The activity coefficients at infinite dilution of a solute (1) in a nonvolatile solvent (3), $\gamma_{13}^{\infty}$, can be calculated, from experimental chromatographic measurements using an insoluble carrier gas (2), by the following:[33,34]

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

in which $n_3$ is the number of moles of the IL packed in the column, $R$ is the ideal gas constant, $T$ is the column's absolute temperature, $V_N$ is the net retention volume of the solute, $p_1^*$ is the 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 pressure at the column outlet, $J_2^3$ is the pressure correction factor, $B_{12}$ is the second virial coefficient of the solute in the carrier gas, and $V_1^{\infty}$ is the solute partial molar volume at infinite dilution. Most of the variables of eq 1 are thermophysical properties of the solute, while $V_N$ and $J_2^3$ can be directly calculated from the data registered during the chromatographic experiments through the following relations:[33,35]

$$V_N = (J_2^3)^{-1} U_f \frac{p_f}{p_0} \frac{T}{T_f} (t_r - t_g) \quad (2)$$

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

where $U_f$, $p_f$, and $T_f$ are the volumetric flow, the pressure, and the temperature measured when the carrier gas is exiting the chromatograph (registered by the flowmeter), $t_r$ and $t_g$ are the retention times of the solute and the non-retained substance (air) introduced into the column along with the solute, respectively, and $p_i$ is the column inlet pressure.

**Gas−Liquid Partition Coefficients.** Another relevant property of solution thermodynamics,[36] the gas−liquid partition coefficient at infinite dilution or distribution



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coefficient, $K_L$, can be calculated from the chromatographic retention times according to the approach proposed by Everett:[33]

$$\ln(K_L) = \ln\left(\frac{c_1^3}{c_1^2}\right) = \ln\left(\frac{V_N\rho_3}{m_3}\right) - \frac{P_0 J_2^3(2B_{12} - V_1^\infty)}{RT} \quad (4)$$

in which $c$ is the molar concentration of the solute, $\rho_3$ is the density of the IL and $m_3$ is the mass of the IL packed into the column.

To provide the necessary thermophysical properties to compute the $\gamma_{13}^\infty$ and $K_L$ values, a detailed review of the literature's available information was carried out. The solutes' vapor pressures and densities were calculated from fitted coefficients using the data available in the literature. The fitted constants are presented in Table S3 of Section SM.3 along with the data sources. To determine the second virial coefficients of the solutes ($B_{11}$) and of the 'solute + carrier gas' mixtures ($B_{12}$), the methods proposed by Tsonopoulus[37,38] and discussed in detail by Poling and co-authors[39] were employed. The critical properties, the acentric factors, and the dipole moments of the solutes, required to calculate the virial coefficients, are listed in Table S4 of Section SM.3, along with the literature references. Regarding the IL density ($\rho_3$), the average values calculated from the available data[40−48] were considered for [$C_8$mim]Cl, whereas the approach proposed by Rebelo et al.,[49] and previously employed by us,[27] was used to estimate the required data for [$C_{12}$mim]Cl and for the [$C_4$mim]Cl/[$C_{12}$mim]Cl equimolar mixture.

## RESULTS AND DISCUSSION

**Activity Coefficients at Infinite Dilution and Gas−Liquid Partition Coefficients.** In the present study, the potential of structurally diverse imidazolium-based ILs to fractionate binary terpene mixtures were evaluated through experimental and modeling approaches. Experimentally, the activity coefficients at infinite dilution, $\gamma_{13}^\infty$, and the gas−liquid partition coefficients, $K_L$, of nineteen monoterpenes in two pure ILs, [$C_8$mim]Cl and [$C_{12}$mim]Cl, and in the equimolar mixture of [$C_4$mim]Cl/[$C_{12}$mim]Cl, were measured by inverse gas chromatography in the temperature range (373.2−453.2) K. The data are listed in Tables S5 and S6.

The results show that chloride-based ILs exhibit strong affinities with the studied monoterpene alcohols and poor interactions with other families of hydrocarbon monoterpenes. This behavior has been shown before for [$P_{6,6,6,14}$]Cl,[18] and it can be ascribed to the formation of strong solute-IL hydrogen-bond interactions. Adding to the dispersive forces present in the cations, it is expected that the highly polar, hydrogen-bond acceptor nature of the chloride anion[50] favors the solvation of solutes presenting hydrogen-bond donor nature, such as alcohols, leading to low $\gamma_{13}^\infty$ values. Monoterpenes hydrocarbons show positive deviations from the ideality, meaning unfavorable solute-IL interactions.

In general, the activity coefficients decrease as the cation alkyl chain length increases (from $C_4$[17] to $C_{12}$). In [$C_4$mim]Cl,[17] considerably higher $\gamma_{13}^\infty$ values are observed, indicating weaker interactions with the monoterpene alcohols, a consequence of the cation shorter alkyl chain length, and higher interaction of chloride anion with it. Besides, the $\gamma_{13}^\infty$ observed for the [$C_4$mim]Cl/[$C_{12}$mim]Cl equimolar mixture are lower than the values registered for the pure [$C_8$mim]Cl for most of the monoterpenes under study, being the variations more substantial for the lower polar solutes, hydrocarbons and ethers.

Apart from representing the equilibrium distribution of a volatile solute between the liquid and vapor phases,[51] $K_L$ also provide insights into the suitability of a nonvolatile solvent, as IL, to fractionate binary mixtures at industrial levels, where the extraction of the target solutes is followed by the recovery of the solvent.[17] In all the cases investigated here, the $K_L$ values indicate the preference of all solutes for the IL phase; but that decreases as the temperature increases, as observed for other ILs.[17,18] Mostly, $K_L$ increase as the cation alkyl chain length increases, suggesting that ILs with larger imidazolium cations retain better the solutes in the liquid phase.

**Separation Factors.** Apart from providing relevant information about the solute−solvent affinity, the $\gamma_{13}^\infty$ can also be used to derive relevant separation factors, as selectivity ($S_{ij}^\infty$), capacity ($k_j^\infty$), and the solvent performance index ($Q_{ij}^\infty$):

$$S_{ij}^\infty = \frac{\gamma_{i3}^\infty}{\gamma_{j3}^\infty} \quad (5)$$

$$k_j^\infty = \frac{1}{\gamma_{j3}^\infty} \quad (6)$$

$$Q_{ij}^\infty = S_{ij}^\infty \cdot k_j^\infty \quad (7)$$

where the subscripts $i$ and $j$ correspond to the target solutes in the mixture, being $j$ the solute with the lower activity coefficient value in the solution.

The selectivity and capacity at infinite dilution are useful parameters to assess the potentialities of a solvent as entrainer to fractionate binary mixtures of miscible compounds through conventional separation processes, such as liquid−liquid extraction or distillation.[52,53] High selectivity values are typically associated with lower numbers of requested stages in industrial separation process, resulting in higher efficiencies.[54] At the same time, very poor capacities might indicate the formation of immiscible phases, increasing the operational costs.[52] Therefore, a potential entrainer candidate should provide a fair compensation between $S_{ij}^\infty$ and $k_j^\infty$, which can be evaluated by the product of these quantities, $Q_{ij}^\infty$.[55]

Experimental selectivities and capacities are presented in Tables S7−S9, while the experimental $Q_{ij}^\infty$ values at 373.2 K are illustrated in Figure 1 (left panel), along with the results predicted by COSMO-RS (right panel). To provide a more comprehensive view of the cation alkyl chain effect, the data reported in our previous study for [$C_4$mim]Cl[17] were also added to Figure 1, along with estimated values of mixtures containing relevant phenolic monoterpenes (eugenol, thymol, and carvacrol) due to their abundance in several EOs.[56−61] Attempts to obtain experimental data for those compounds were carried out, but no reliable data was achieved due to the long retention times, a consequence of the strong interactions of those probes with the solvent.

In general, separation factors show that the Cl-based ILs are promising alternatives to fractionate alcohol/non-alcohol mixtures, where [$C_{12}$mim]Cl is the best option for mixtures containing geraniol or $\beta$-citronellol, and [$C_8$mim]Cl or [$C_4$mim]Cl/[$C_{12}$mim]Cl give the best performance for mixtures containing other monoterpene alcohols. For all ILs, the highest experimental $Q_{ij}^\infty$ values are observed for $\alpha$-pinene/geraniol, reaching values higher than 1000. The high polarity of the chloride anion is linked with the low $\gamma_{13}^\infty$ observed for



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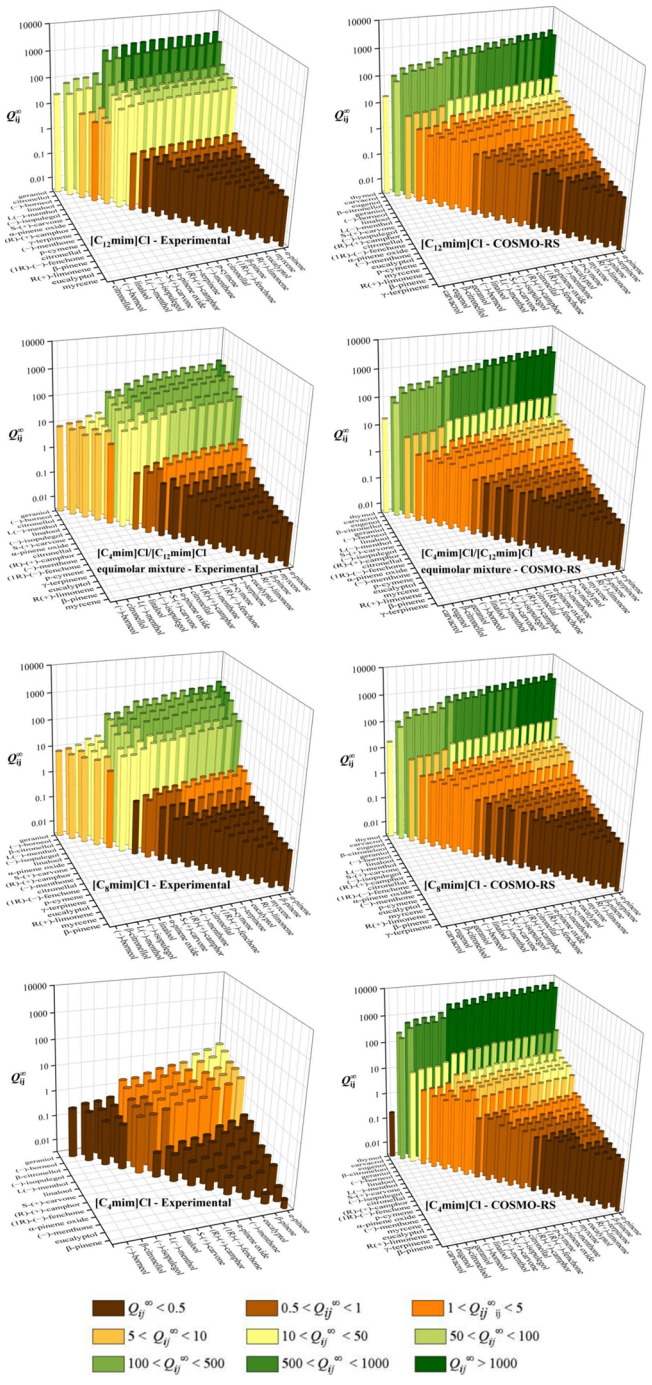


**Figure 1.** Experimental and predicted $Q_{ij}^{\infty}$ values, at 373.2 K, for the binary mixtures of terpenes in [$C_{12}$mim]Cl, [$C_4$mim]Cl/[$C_{12}$mim]Cl equimolar mixture, [$C_8$mim]Cl, and [$C_4$mim]Cl. The $Q_{ij}^{\infty}$ values for [$C_4$mim]Cl were extrapolated from the available $\gamma_{13}^{\infty}$ data.[17]

alcohols, and with the high values of the less polar solutes (e.g., hydrocarbons and ethers), favoring the fractionation of these mixtures. In this sense, the chloride-based ILs showed very poor solvent performance indices for the fractionation of mixtures containing only hydrocarbons ($Q_{ij}^{\infty}$ < 0.5), mainly because of the low-capacity values. As evidenced in our previous studies,[17,18] the search for an appropriate entrainer for the fractionation of hydrocarbon terpenic mixtures is challenging, and by tailoring the alkyl chain length of the cation for imidazolium chloride IL, no significative improvements were achieved. Similarly, modest experimental $Q_{ij}^{\infty}$ values were registered for the mixtures of hydrocarbons and ethers, ketones, or aldehydes monoterpenes.

**COSMO-RS.** COSMO-RS is a robust predictive tool capable of estimating thermodynamic and equilibrium properties of pure compounds and mixtures.[29,62,63] Among a broad range of applications, COSMO-RS has been widely used to estimate $\gamma_{13}^{\infty}$ data of organic solutes in ILs.[17,18,64−67] In this study, the model was used to provide a qualitative description of the solvent performance indices. To better compare the experimental and predicted sets, each $Q_{ij}^{\infty}$ interval from the color scheme presented in Figure 1 is linked to a different scale numbered from 1 to 9, where scale 1 corresponds to the separation presenting $Q_{ij}^{\infty}$ < 0.5, and scale 9 represents those with $Q_{ij}^{\infty}$ > 1000. COSMO-RS predicts the correct scale for 26% of the evaluated binary terpene mixtures, and this percentage increases to 49 and 67% assuming up to one and two order scale difference, respectively. As detailed in the Experimental Section, all the conformers generated with the COSMOconf software were used in the COSMO-RS calculations. Alternatively, the lowest energy conformation instead of multiple conformers has also been adopted in the literature.[67,68] This approach has also been tested in this study, but slightly poorer global performances were obtained compared to when multiple conformers are used.

As shown in Figure 1, the model detects the poor performance (scales 1 to 3) of ILs to fractionate mixtures containing low to moderate polar solutes, predicting the correct scale for 53% of those. For binary mixtures involving alcohols, the model reached only 6% of the correct $Q_{ij}^{\infty}$ interval scales for the analyzed mixtures, frequently underestimating the performance indices, particularly for mixtures containing aliphatic primary monoterpene alcohols as geraniol or $\beta$-citronellol. No significative differences were observed in the predicted $Q_{ij}^{\infty}$ profiles for [$C_8$mim]Cl and the equimolar mixture of [$C_4$mim]Cl and [$C_{12}$mim]Cl.

Despite the overall lack of accuracy, COSMO-RS captures the global scenario of the $Q_{ij}^{\infty}$ values revealed by the experimental data. The model can predict that the poorest performance indices occur for the mixtures of hydrocarbons, while the highest $Q_{ij}^{\infty}$ values (except for the mixtures with phenolics) are observed for hydrocarbon/alcohol mixtures. Besides, COSMO-RS delivers intermediate $Q_{ij}^{\infty}$ values for the mixtures of hydrocarbons and other monoterpenoids (i.e., ketones, aldehydes, ethers), which is, in many cases, confirmed by the experimental data. COSMO-RS's ability in predicting the correct $Q_{ij}^{\infty}$ order is useful for preliminary screening ILs as entrainers for the fractionation of EOs. Moreover, the predictive nature of COSMO-RS also allows the estimation of separation factors for any solute, such as eugenol, thymol, and carvacrol. For those phenolic monoterpenes, the high predicted $Q_{ij}^{\infty}$ values ($Q_{ij}^{\infty}$ > 100 in 66% of the cases) suggest that the addressed ILs are excellent options to be explored as separation agents. Indeed, the strong affinity between these compounds and the imidazolium chloride-IL agrees with the experimental findings, where no well-defined peak was observed during the chromatographic experiments even after several hours.

Since COSMO-RS was shown to be a valuable tool for a qualitative description of the experimental separation factors addressed above, the model was further employed to screen other potential separation agents for terpene mixtures. First, the effect of replacing the chloride anion by a much less polar anion, tetrafluoroborate ($[BF_4]^-$),[50] was examined (Figure


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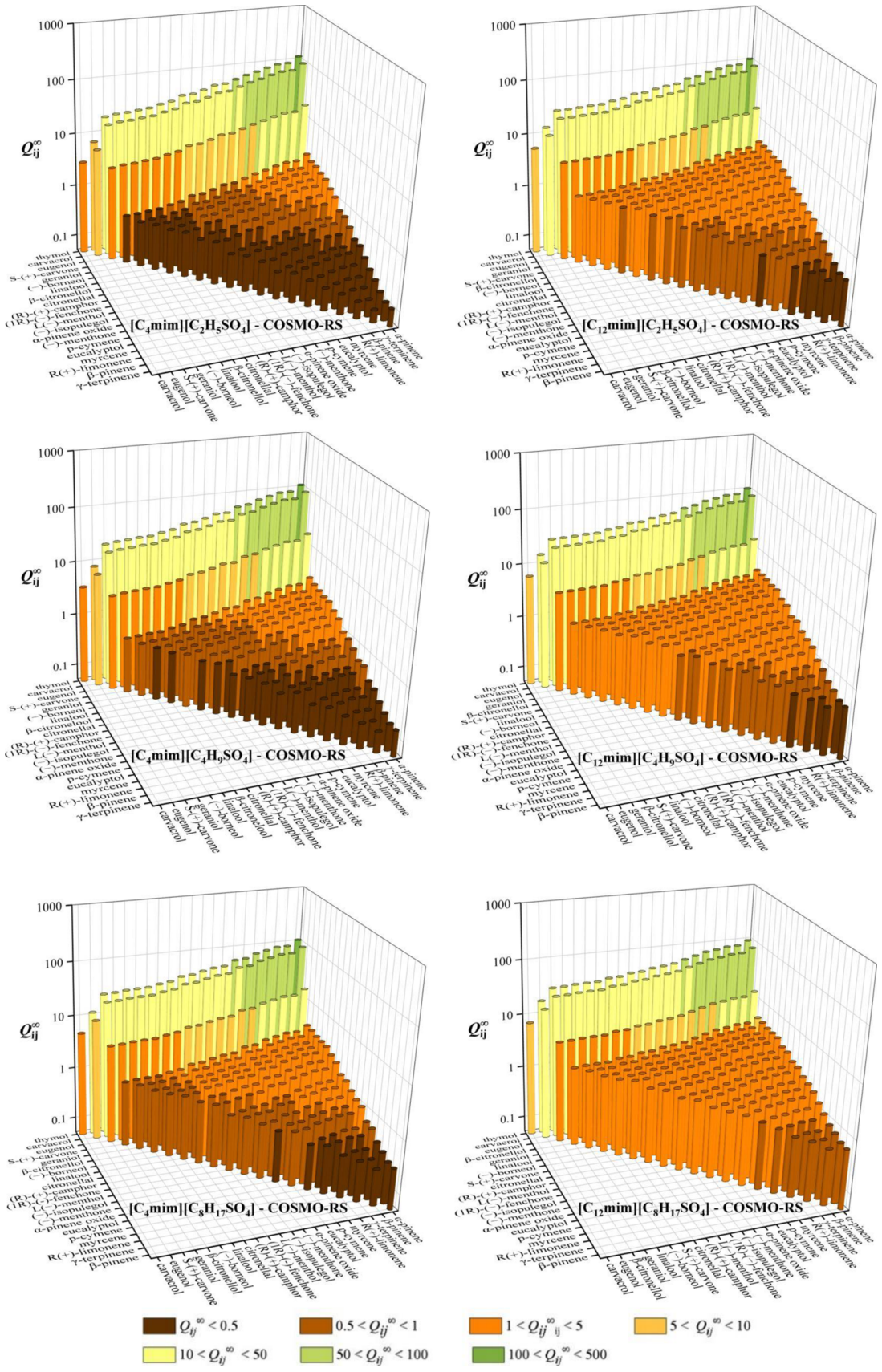


**Figure 2.** Predicted $Q_{ij}^{\infty}$ values for the terpene mixtures in $[C_4mim][C_2H_5SO_4]$, $[C_{12}mim][C_2H_5SO_4]$, $[C_4mim][C_4H_9SO_4]$, $[C_{12}mim][C_4H_9SO_4]$, $[C_4mim][C_8H_{17}SO_4]$, and $[C_{12}mim][C_8H_{17}SO_4]$, at 373.2 K.



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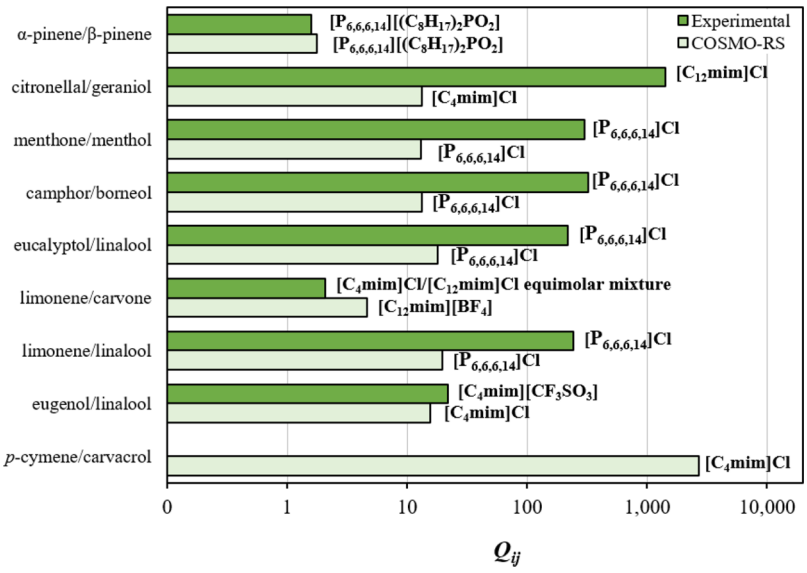


**Figure 3.** Overview of the experimental and predicted (with COSMO-RS) $Q_{ij}^{\infty}$ values of the best ILs to fractionate each EO representative terpene mixture.[17,18]

S1). $[C_8mim][BF_4]$, which is equivalent to the equimolar mixture, generally performs better than $[C_4mim][BF_4]$ and worse than $[C_{12}mim][BF_4]$. Like in the previous cases, the poorest performance indices were registered for the fractionation of hydrocarbon mixtures, while the highest solvent performance indices were computed for mixtures containing phenolics: eugenol, thymol, and carvacrol. Nonetheless, the overall $Q_{ij}^{\infty}$ values are much lower than those predicted for the imidazolium chloride ILs. On the other hand, the $[BF_4]$-based ILs delivered better performances for the mixtures of hydrocarbons with ketones or citronellal than those with alcohols, which is the opposite of the trend observed in the chloride-based ILs.

After evaluating the effect of the imidazolium cation chain length in ILs with $Cl^-$ and $[BF_4]^-$ anions, the anion alkyl chain length tailoring was addressed. Thus, the separation factors of different monoterpene binary mixtures in three IL with the same imidazolium cations ($[C_4mim]^+$, $[C_8mim]^+$~ equimolar $[C_4mim]/[C_{12}mim]^+$, and $[C_{12}mim]^+$) and three sulfate-based anions with different alkyl-chains ($[C_2H_5SO_4]^-$, $[C_4H_9SO_4]^-$, and $[C_8H_{17}SO_4]^-$) were calculated using the COSMO-RS model. Predicted $Q_{ij}^{\infty}$ are presented in Figures 2 and S2 of the SM.

For most of the studied mixtures and for ILs with a common $SO_4$-based anion, an increase in the alkyl cation size leads to a higher predicted solvent performance indices. Also, higher $Q_{ij}^{\infty}$ values were obtained by increasing the anion size from $[C_2H_5SO_4]^-$ to $[C_8H_{17}SO_4]^-$ (for ILs with the same cation) for most terpene mixtures, except those containing phenolics, which present similar patterns in all the studied $SO_4$-based IL. Fixing $[C_4mim]^+$, the number of terpene mixtures presenting $Q_{ij}^{\infty} > 1$ increased from 57% in $[C_4mim][C_2H_5SO_4]$ to 87% in $[C_4mim][C_8H_{17}SO_4]$ and similar trends are observed for the $SO_4$-based ILs with other imidazolium cations (Table S10). In the review by Marciniak,[69] it is clearly stated that the increase of the alkyl chain length, both in the cation or anion, causes a decrease of the selectivity and an increase of the capacity. In this study, we combined selectivity and capacity into the performance index, and COSMO-RS shows that increasing the alkyl chain of the cation or anion improves the overall performance.

Overall, $SO_4$-based ILs delivered the best results for the mixtures containing eugenol, carvacrol, and thymol, while the poorest $Q_{ij}^{\infty}$ values were registered for the mixtures containing only hydrocarbon terpenes. For most of the analyzed binary mixtures, the replacement of chloride by less polar anions ($[BF_4]^-$, $[C_2H_5SO_4]^-$, $[C_4H_9SO_4]^-$, or $[C_8H_{17}SO_4]^-$) does not improve the investigated separations, with $BF_4$-based ILs having the poorest performance.

**EOs Mixtures.** Among the terpene studied, some pairs represent the major components found in important EOs. An overview of some representative terpene mixtures, their correspondent EO, and the available experimental solvent performance indices (at 373.2 K) is presented in Table S11. The experimental and predicted (with COSMO-RS) $Q_{ij}^{\infty}$ values for the best entrainer (IL) for each EO model mixture are summarized in Figure 3. COSMO-RS was, at this point, used to scan all the ILs investigated experimentally (this study and refs 17, 18). The best results obtained for each separation are included in Figure 3, along with the best experimental results.

Very poor experimental $Q_{ij}^{\infty}$ values were found for the fractionation of $\alpha$-pinene/$\beta$-pinene mixture with all ILs studied so far, being the best values registered for phosphonium-based ILs.[18] This behavior is well captured by COSMO-RS. A considerably higher efficiency was found with Carbowax 6000 ($Q_{ij}^{\infty} = 7.00$).[70] The fractionation of this monoterpenes mixture is particularly attractive at an industrial scale, since these compounds are widely found in pinus EOs[55,71,72] and turpentine, an important byproduct of the pulp and paper industry.[73] Nevertheless, the low available $Q_{ij}^{\infty}$ values reveal that the separation of these structurally similar compounds through liquid−liquid extraction or distillation processes is yet quite challenging.

In the case of mixtures containing alcohols (menthone/menthol, camphor/borneol, eucalyptol/linalool, and limonene/linalool), very good experimental performance indices were found for most of the chloride-based ILs, being the best values registered for $[P_{6,6,6,14}]Cl$ ($Q_{ij}^{\infty} > 218$). Again, COSMO-


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RS is capable of identifying $[P_{6,6,6,14}]Cl$ as the most suitable option as separation agent. Regarding citronellal/geraniol, $[C_{12}mim]Cl$ and $[C_4mim]Cl$ were the best ILs identified experimentally and using COSMO-RS, respectively. For this separation, which is representative of citronella EO,[74,75] an excellent performance index was obtained with $[C_{12}mim]Cl$ ($Q_{ij}^{\infty}$ = 1435). However, no experimental data with the phosphonium ILs is available to compare.

For the limonene/carvone mixture, the main constituents of some spearmint species EOs,[76−79] low experimental $Q_{ij}^{\infty}$ values were found (lower than 2.1), suggesting that limited efficiencies are expected when using $[C_4mim][CH_3CO_2]$, $[P_{6,6,6,14}][(C_8H_{17})_2PO_2]$, or Cl-based ILs as separation agents in industrial separation processes. COSMO-RS confirms the poor performances indices with chloride imidazolium ILs ($Q_{ij}^{\infty}$ < 2.5), and gives slightly better predictions with $BF_4$-based and $SO_4$-based ILs, particularly those with the cation $[C_{12}mim]^+$.

Although only one experimental data point was reported for the eugenol/linalool mixture (in $[C_4mim][CF_3SO_3]$),[17] this mixture was also taken into account here due to its relevance in different cinnamon EO profiles.[57,80,81] Reasonable solvent performance indices were estimated by COSMO-RS for the imidazolium chloride ILs ($Q_{ij}^{\infty}$ > 6.8) and $SO_4$-based ILs ($Q_{ij}^{\infty}$ > 3.5), yet lower than the experimental value ($Q_{ij}^{\infty}$ = 21.7).

Another relevant phenolic terpene mixture, *p*-cymene/carvacrol, commonly found in the EOs from oregano species,[58,72,82] was also considered in the overview presented in Figure 3, despite the absence of experimental data. Chloride-based ILs are the most promising alternatives, achieving remarkably high solvent performance indices especially for $[C_4mim]Cl$ ($Q_{ij}^{\infty}$ = 2688).

Even though EOs are abundant sources of many value-added monoterpenes, the literature addressing separation and purification technologies to obtain terpenes from their natural matrices is somehow scarce.[83] And even though the use of ILs as separation agents in liquid−liquid extraction[13,14,84] or extractive distillation[15,16] processes has been investigated, most studies focus only on the deterpenation of citrus EOs, represented by limonene/linalool binary mixture. Nevertheless, the results found in this study and previous studies from our group[17,18] suggest that some ILs are potential separating agents to fractionate terpene mixtures found in the diverse EOs, such as citronellal/geraniol, eucalyptol/linalool, camphor/borneol, menthone/menthol, and *p*-cymene/carvacrol. Moreover, despite its limitations in providing a quantitative picture of the $Q_{ij}^{\infty}$ values, COSMO-RS can capture their overall trends for the studied monoterpene mixtures in many of the analyzed cases, identifying the best IL in five of the eight representative mixtures (Figure 3). Therefore, the model is an adequate tool for pre-screening ILs for specific separations, particularly when no experimental data is available.

## CONCLUSIONS

This study evaluates different ILs to isolate the main components in relevant EOs. Experimental activity coefficients at infinite dilution and gas−liquid partition coefficients of 19 terpenes in three chloride-based ILs were derived from the chromatographic experiments, allowing the calculation of separation factors for many binary terpene mixtures. The COSMO-RS model was applied to represent the acquired separation factors and to screen other ILs to perform the fractionation of important EO mixtures.

Experimentally, in most cases, monoterpene alcohols strongly interact with the chloride-based ILs ($\gamma_{13}^{\infty}$ < 1). In contrast, the opposite behavior is observed for the other families of monoterpenes (i.e., hydrocarbons, ketones, ethers, and aldehydes). In general, $\gamma_{13}^{\infty}$ decreases as the alkyl chain of the imidazolium cation increases, while the opposite trend occurs for the $K_L$ values. Moreover, the experimental separation factors demonstrate that $[C_8mim]Cl$, $[C_{12}mim]Cl$, and equimolar $[C_4mim]Cl/[C_{12}mim]Cl$ mixtures are promising options to fractionate the mixtures of the solutes with different polarities, particularly hydrocarbon/alcohol mixtures, where $Q_{ij}^{\infty}$ > 50 were often obtained. On the contrary, the worst separation performances are typically observed for the mixtures of hydrocarbon monoterpenes, which have similar nature. Regarding the model EO mixtures, the available experimental data suggests that chloride-based ILs, particularly $[P_{6,6,6,14}]Cl$, are promising options to fractionate oils containing alcohol monoterpenes, such as basil, citrus, and mentha species.

COSMO-RS captures the global trends observed in experimental $Q_{ij}^{\infty}$ values, identifying that the imidazolium Cl-based ILs present the best and worst separation performance for the hydrocarbon/alcohol and hydrocarbon/hydrocarbon mixtures, respectively. Besides, the model distinguished the most promising ILs to separate five of the eight model EO mixtures, which is good performance for a pure predictive approach. The results suggest that COSMO-RS is suitable for the preliminary screening separation agents for fractionating EO mixtures, particularly when no experimental data is available. The results from this study encourage further investigation into the application of imidazolium and phosphonium ILs as separation agents to isolate and purify monoterpenes from EOs.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.2c04637.

General information of the chemicals investigated in this study; detailed description of the procedures employed and thermodynamic background; experimental activity coefficients at infinite dilution, gas−liquid partition coefficients and separation factor; COSMO-RS $Q_{ij}^{\infty}$ predictions; summary of the experimental solvent performance index available for different terpene mixtures representative of common essential oils (PDF)

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### Notes

The authors declare no competing financial interest.

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