

Selection of Ionic Liquids to be Used as Separation Agents for Terpenes and Terpenoids

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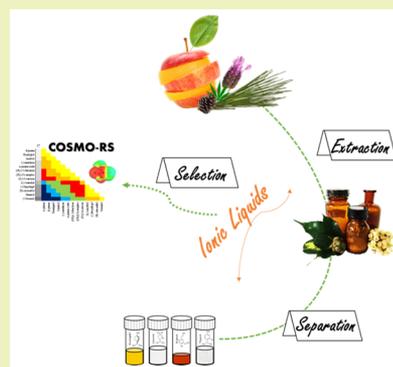
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S Supporting Information

ABSTRACT: In this work, ionic liquids are evaluated for the first time as solvents for extraction and entrainers in separation processes involving terpenes and terpenoids. For that purpose, activity coefficients at infinite dilution, γ_{13}^{∞} , of terpenes and terpenoids, in the ionic liquids $[\text{C}_4\text{mim}]\text{Cl}$, $[\text{C}_4\text{mim}][\text{CH}_3\text{SO}_3]$, $[\text{C}_4\text{mim}][(\text{CH}_3)_2\text{PO}_4]$ and $[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3]$ were determined by gas–liquid chromatography at six temperatures in the range 398.15 to 448.15 K. On the basis of the experimental values, a correlation of γ_{13}^{∞} with an increase of the solubility parameters is proposed. The infinite dilution thermodynamic functions were calculated showing the entropic effect is dominant over the enthalpic. Gas–liquid partition coefficients give indications about the recovery and purification of terpenes and terpenoids from ionic liquid solutions. Presenting a strong innovative character, COSMO-RS was evaluated for the description of the selectivities and capacities, showing to be a useful tool for the screening of ionic liquids in order to find suitable candidates for terpenes and terpenoids extraction, and separation. COSMO-RS predictions show that in order to achieve the maximum separation efficiency, polar anions should be used such as bis(2,4,4-trimethylpentyl)phosphinate or acetate, whereas high capacities require nonpolar cations such as phosphonium.

KEYWORDS: Terpenes, Terpenoids, Ionic liquids, Activity coefficients at infinite dilution, COSMO-RS, Selectivity, Capacity



INTRODUCTION

Essential oils are mixtures of volatile compounds isolated from animal and about 300 different plants species. Per year, 100 000 tons of volatile essential oils, with a value of about 1 billion US\$, are produced worldwide for the food, flavor and fragrance industries. Apart from the volatile oils production, 250 000–300 000 tons of turpentine are also produced, from which about 100 000 tons are used for the production of terpenes and terpenoids.¹

Terpenes and terpenoids have been used since Egyptian civilization² and their importance in both nature and human applications is enormous. The main reason for this great use is the abundance and diversity of these compounds in nature. Using a five carbon building block, the isoprene, nature creates an array of compounds with a wide range of structural variations and a vast number of applications.³ Structurally, terpenes are unsaturated hydrocarbons and they can also occur as oxygenated derivatives, called terpenoids.⁴

To be applied in food, perfumery, medicines and cosmetics, pure terpenes and terpenoids must be extracted from natural sources.² Despite their abundance, they are usually present in low concentrations, so they tend to be expensive or even uneconomic to exploit.³ However, when in high concentrations, terpenes and

terpenoids mixtures can present undesirable properties, and then the deterpenation is imperative.⁵

For the production of pure compounds from natural materials, or for the deterpenation, the extraction of terpenes and terpenoids is of the utmost importance, being an area regarding eagerly for new technological developments. Vacuum and steam-distillations, membrane processes, supercritical extraction, solvent (or liquid–liquid) extraction and chromatography are the techniques most used to remove hydrocarbons from essential oils.⁶ The solvent extraction is preferred, because this method requires less energy than processes such as distillation and supercritical fluid extraction, while retaining the most volatile aliphatic chemicals⁷ and preserving the organoleptic properties of the original oil.

To the best of our knowledge, the first study on terpene and terpenoids extraction dates back to 1959,⁸ and since then a vast number of works were published in this field.³ Regarding the

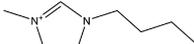
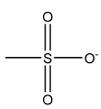
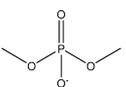
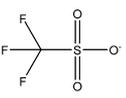
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Table 1. Name, Structure, Abbreviation, Supplier, Molar Mass (M), Melting Point (T_{MP}) and Purity of the Investigated Ionic Liquids

Chemical Formula		Chemical Name	Supplier	M (g·mol ⁻¹)	T_{MP} (K)	Purity (mass %)
Cation	Anion					
	Cl ⁻	1-butyl-3-methylimidazolium chloride, [C ₄ mim]Cl	IoLiTec	174.67	341.95 ³⁷	99
		1-butyl-3-methylimidazolium methanesulfonate, [C ₄ mim][CH ₃ SO ₃]	IoLiTec	234.32	≈ 353.15 ³⁸	99
		1-butyl-3-methylimidazolium dimethyl phosphate, [C ₄ mim][(CH ₃) ₂ PO ₄]	IoLiTec	264.26	< 253.15	98
		1-butyl-3-methylimidazolium trifluoromethanesulfonate, [C ₄ mim][CF ₃ SO ₃]	IoLiTec	288.29	289.15 ³⁹	99

liquid–liquid extraction, water and several organic solvents have been investigated, as alcohols, acetonitrile, glycols and amino-ethanol.⁶ Lately, another class of compound with exceptional properties have emerged as potential substituent for organic solvents, in the terpenes and terpenoids extraction, the ionic liquids (ILs).^{9–11}

Ionic liquids are a neoteric class of compounds with adjustable characteristics as the miscibility and the polarity and exceptional properties as the nonvolatility, chemical and thermal stability, large liquid temperature range and high solvating capacity.¹² Many recent reviews summarize the large range of applications of ionic liquids in organic synthesis, catalysis, electrochemistry and separation technology.^{13,14}

To exploit fully the ILs potential in extraction and separation processes of terpenes and terpenoids and, in order to avoid a large number of experimental liquid–liquid extractions, screening methods to evaluate the best solvents are necessary. Solute–solvent interactions, selectivities and capacities can be derived from activity coefficients at infinite dilution (γ_{13}^{∞}).^{15,16} These can be determined from retention times using gas–liquid chromatography (GLC),¹⁷ and are related to the relative strength of intermolecular interaction of the solute with the ionic liquid.

Prediction tools can also be used to the same end. COSMO-RS (COnductor-like Screening MOdel for Real Solvents) is a quantum chemical approach, proposed by Klamt and Eckert¹⁸ and used by several authors,^{19,20} for the a priori prediction of infinite dilution activity coefficients and other thermophysical data using only structural information on the molecules.

This work reports on the application of infinite dilution activity coefficient data to select ionic liquids able to promote the separation and purification of terpenes and terpenoids. Thus, the γ_{13}^{∞} of 17 terpenes and terpenoids, in the ionic liquids composed by the cation 1-butyl-3-methylimidazolium, [C₄mim]⁺, and the anions: chloride, Cl⁻; dimethyl phosphate, [(CH₃)₂PO₄]⁻; methanesulfonate, [CH₃SO₃]⁻, and trifluoromethanesulfonate, [CF₃SO₃]⁻, are reported. The measurements were carried out using gas–liquid chromatography in the temperature range (398.15 to 448.15) K. The ionic liquids were chosen in order to

evaluate the effect of the polarity of the anion and variations in their structure. The new data here gathered were used to evaluate the ability of COSMO-RS in the description of the selectivities and capacities for these compounds, and the model was then applied to screen different IL cations and anions for terpenes and terpenoids separation.

EXPERIMENTAL SECTION

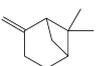
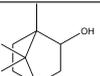
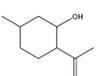
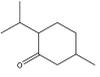
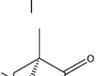
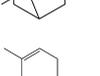
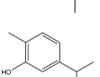
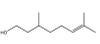
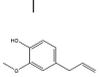
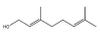
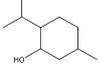
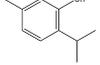
The properties of the ionic liquids used in this work are presented in Table 1, whereas the terpenes and terpenoids description is available in Table 2 and Table S1. The procedures for ILs purification and characterization are given in the Supporting Information. The water content was found to be below 300 ppm for all IL samples. Terpenes and terpenoids were used without any further purification. The infinite dilution activity coefficients were estimated from retention times measurements performed using a PerkinElmer Clarus 500 gas chromatograph through the GLC method detailed elsewhere.^{21,22} TURBOMOLE 6.1 program package was used to generate the COSMO-RS input files.²³ The parametrization adopted was BP_TZVP_C30_1401 (COSMOconfX v3.0, COSMOlogic GmbH & Co KG, Leverkusen, Germany).

The detailed experimental steps and the theoretical foundations for infinite dilution activity coefficients calculation are displayed in the Supporting Information, as well as the frameworks for molar excess thermodynamic functions or important separation quantities such as gas–liquid partition coefficients, selectivity or capacity.

RESULTS AND DISCUSSION

Activity Coefficients at Infinite Dilution. The experimental measurements of the activity coefficients at infinite dilution of terpenes and terpenoids in ILs were carried out between 398.15 and 448.15 K, with intervals of 10 K, and the average values at each temperature are presented in Table S2 of the Supporting Information. High temperatures were adopted to avoid long retention times of solutes, and to prevent the solidification of the ionic liquids used inside the column. To understand better and explore the data, a comparison at a fixed temperature, 408.15 K, is presented in Figure 1. This temperature was chosen because it is the lowest temperature at

Table 2. Names, Structures, Supplier, Molar Mass (M), Boiling Points (T_{BP}) and Mass Fraction Purities of the Terpenes and Terpenoids Used

Chemicals	Supplier	CAS	M (g·mol ⁻¹)	T_{BP} (K) ⁴⁰	Mass fraction purity ^a	
Terpenes						
α -pinene		Sigma-Aldrich	80-56-8	136.237	429.29	98%
β -pinene		Sigma-Aldrich	18172-67-3	136.237	439.19	99%
Terpenoids						
(-)-borneol		Fluka	464-45-9	154.252	485.80	≥99%
(-)-Isopulegol		SAFC	89-79-2	154.252	480.98	≥98%
(-)-menthone		Fluka	14073-97-3	154.252	483.15	≥99%
(1R)-(-)-fenchone		Aldrich	7787-20-4	152.236	466.15	≥98%
(1R)-(+)-camphor		Aldrich	464-49-3	152.236	480.55	98%
(S)-(+)-carvone		Merck	2244-16-8	150.221	504.15	96%
Carvacrol		SAFC	499-75-2	150.221	510.15	99%
DL-citronellol		Sigma	106-22-9	156.268	496.40	≈95%
Eucalyptol		Aldrich	470-82-6	154.252	449.55	99%
Eugenol		Aldrich	97-53-0	164.204	526.35	99%
Geraniol		Sigma-Aldrich	106-24-1	154.252	503.15	98%
L(-)-menthol		Acros	2216-51-5	156.268	487.40	99.7%
Linalool		Aldrich	78-70-6	154.252	470.15	97%
Thymol		Sigma	89-83-8	150.221	505.65	≥99.5%
α -pinene oxide		Aldrich	1686-14-2	152.236	489.51	97%

^aDeclared by the supplier.

which data are available for all the solutes studied in, at least, one ionic liquid.

As shown in Figure 1, α -pinene and β -pinene show the weakest interactions with the ILs studied. This was expected because all

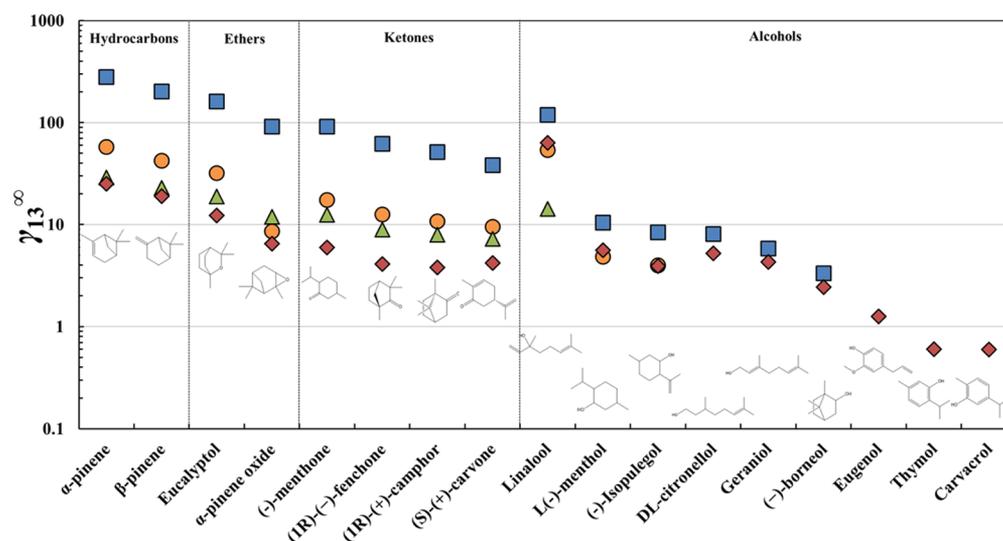


Figure 1. Activity coefficients at infinite dilution of terpenes and terpenoids in the ILs studied, at 408.15 K. \square , $[\text{C}_4\text{mim}]\text{Cl}$; \circ , $[\text{C}_4\text{mim}][\text{CH}_3\text{SO}_3]$; Δ , $[\text{C}_4\text{mim}][(\text{CH}_3)_2\text{PO}_4]$; \diamond , $[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3]$.

the ionic liquids used present polar anions and thus, interact better with polar solutes as terpenoid alcohols, whereas the interactions with hydrocarbons (terpenes), and terpenoid ethers and ketones are weaker presenting higher values of activity coefficients at infinite dilution.

The terpenoid linalool is a clear exception, presenting an increase in the activity coefficients at infinite dilution and, additionally, a change in the ILs trend, when compared with the other alcohols. Trying to rationalize this apparent outlier, the σ -profiles of all ILs and solutes in their most stable form were computed by COSMO-RS, and the results are presented in Figure S1 of the Supporting Information. The alcohols σ -profiles show that linalool is the only one that does not present an H-bond donor character. Because the ILs anions have an H-bond acceptor character, the interactions are weaker and, consequently, the γ_{13}^∞ increases. Moreover, the change in the ILs trend suggests that in this case the anion–cation interaction is dominant face to the solute–anion interaction.

Because of the long retention times, and to the TCD detector sensitivity limit, the activity coefficients at infinite dilution of a few alcohols, in some ionic liquids, were not possible to measure. However, in $[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3]$, the least polar IL,²⁴ all solutes were measured. No significant differences were observed between the aromatic and the aliphatic terpenoids, suggesting that the cyclical structure does not have a relevant impact in the activity coefficients at infinite dilution in the aromatic imidazolium ILs here investigated.

In our previous work,²⁵ measurements of γ_{13}^∞ for organic solutes with the same ILs were carried out. Taking into account the functional groups, the same trend of γ_{13}^∞ was found: hydrocarbons > ethers > ketones > alcohols. Moreover, the ILs trend observed for the infinite dilution activity coefficients magnitude was $[\text{CF}_3\text{SO}_3]^- < [(\text{CH}_3)_2\text{PO}_4]^- < [\text{CH}_3\text{SO}_3]^- < \text{Cl}^-$, which is in good agreement with the polarity trend described by Cláudio et al.²⁴

The dependency with the temperature is presented in Figure S2 of the Supporting Information. For most solutes, there is a linear increase or decrease in the natural logarithm of γ_{13}^∞ with the reciprocal temperature. The compounds (–)-menthone, (S)-(+)-carvone and (1R)-(+)-camphor in $[\text{C}_4\text{mim}]\text{Cl}$; (–)-menthone, geraniol and (1R)-(+)-camphor in $[\text{C}_4\text{mim}][\text{CH}_3\text{SO}_3]$;

and (1R)-(–)-fenchone and eucalyptol in $[\text{C}_4\text{mim}][(\text{CH}_3)_2\text{PO}_4]$ and $[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3]$ present almost an independent behavior of the logarithm of γ_{13}^∞ with the reciprocal temperature, and thus their enthalpy of solution is close to zero.

Despite the large number of studies published on the measurement of infinite dilution activity coefficients of solvents in ionic liquids, to the best of our knowledge no data for infinite dilution activity coefficients of terpenes and terpenoids was previously reported using ILs as a stationary phase, and no comparison is possible.

In an attempt to systematize the data collected here, correlations of the activity coefficients at infinite dilution of the terpenes and terpenoids measured with some of their properties (e.g., dipolar moment, solubility parameter, molar volume) were evaluated. The most promising results are reported on Figure 2

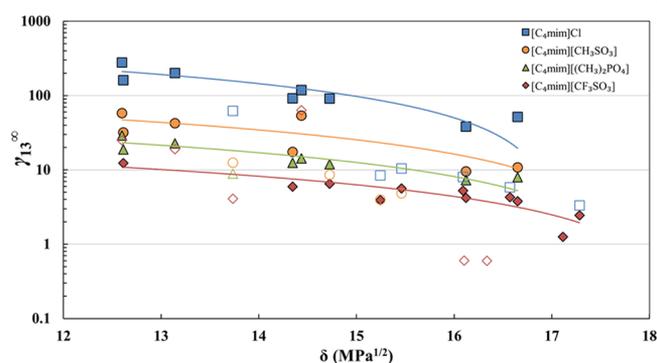


Figure 2. Activity coefficients at infinite dilution as a function of the solubility parameters (calculated through²⁶) of terpenes and terpenoids in the ILs studied, at 408.15 K. Empty symbols were not used in the fit.

for the correlation with the solubility parameters calculated through the relation presented by Goharshadi and Hesabi.²⁶ Results show a decrease of the activity coefficient at infinite dilution with the increase of the solubility parameter. Additionally, the different ILs presents almost parallel trend lines, suggesting a predictive character to be explored as soon as more data are available.

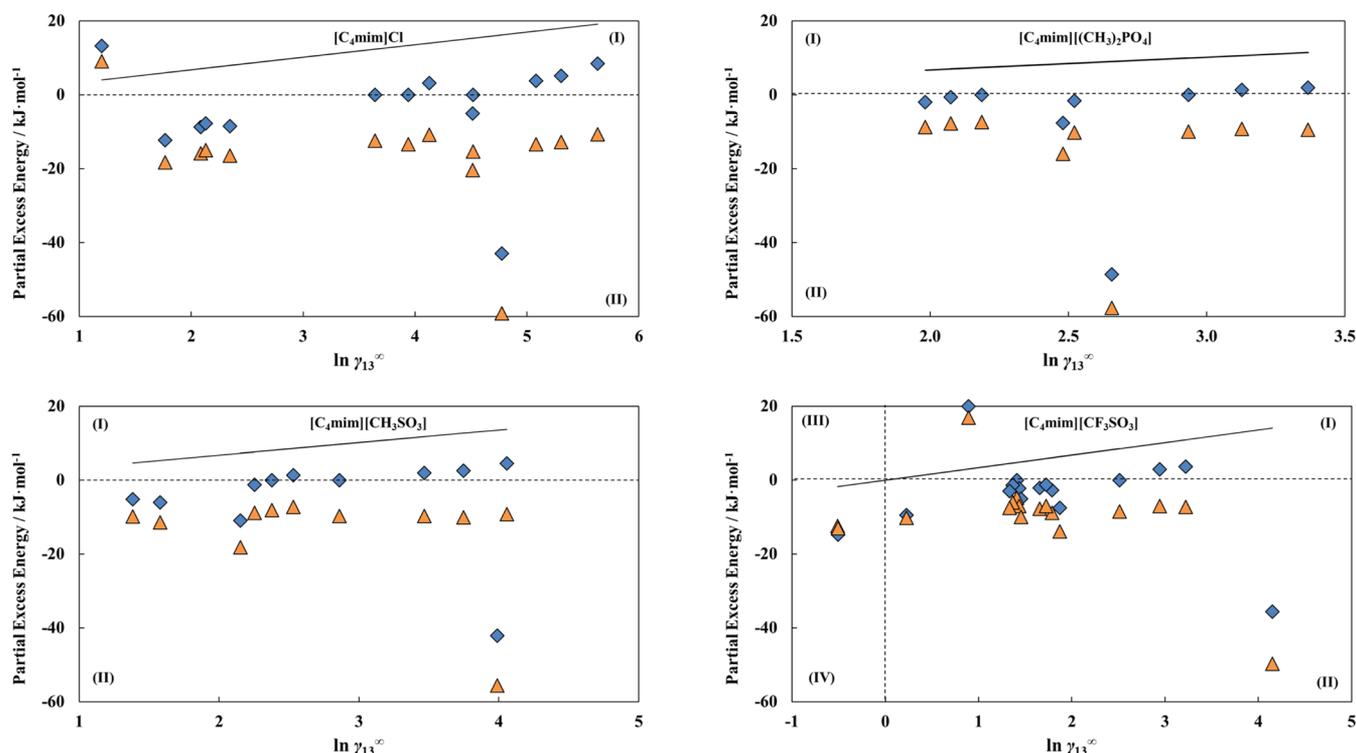


Figure 3. Partial molar excess energies at infinite dilution as a function of the natural logarithm of the activity coefficients at infinite dilution of the terpenes and terpenoids in the ILs study, at 408.15 K. The full line represents $\bar{G}_m^{E,\infty}$ and the symbols correspond to \diamond , $\bar{H}_m^{E,\infty}$ and Δ , $T_{ref}\bar{S}_m^{E,\infty}$.

Thermodynamic Functions at Infinite Dilution. To obtain additional information concerning the interactions between the solutes and the ionic liquids, the partial excess molar properties at infinite dilution were analyzed. The Gibbs energy, enthalpy and entropy, for terpenes and terpenoids in the investigated ILs at $T = 408.15$ K were calculated through the γ_{13}^{∞} values, and the results are listed in Table S3 of the [Supporting Information](#). As mentioned before, there are some solutes in some ILs that present a small variation with the temperature and hence, in those cases, the partial molar excess enthalpy at infinite dilution is close to zero.

The partial molar excess properties as a function of γ_{13}^{∞} are presented in [Figure 3](#). As can be seen, two different areas can be distinguished for ILs composed by the more polar anions (Cl^- , $[\text{CH}_3\text{SO}_3]^-$, $[(\text{CH}_3)_2\text{PO}_4]^-$), and three areas for the IL $[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3]$. Region I and II, common to all ILs studied, represents the ILs–organic solutes systems with positive deviations to Raoult’s law, γ_{13}^{∞} ($\bar{G}_m^{E,\infty}$) > 1. When $\bar{H}_m^{E,\infty}$ is also positive, region I, no particular affinity between ILs and solutes molecules is expected, as for hydrocarbons, ketones and ethers. Because of the weak interaction, these mixtures have potential to the formation of two immiscible phases. In region II both enthalpy and entropy are negative, clearly indicating the dominance of the entropic over the enthalpic effect. Indeed, in both regions, the partial excess enthalpy is close to zero, and the entropic effect is always dominant.

$[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3]$ presents also region IV, with negative deviations from Raoult’s law ($\gamma_{13}^{\infty} < 1$). This region is characterized by favorable interactions between the solutes and the ILs, related with spontaneous dissolution, and consequently the enthalpic effect is dominant. The only solutes belonging to that region are carvacrol and thymol, both presenting strong polarity, where all the partial excess molar properties investigated are negative, showing that the HB between carvacrol and thymol,

and the anion $[\text{CF}_3\text{SO}_3]^-$ is favorable. The terpenoid linalool, highlighted before due to the absence of an H-bond donor region character, shows an extremely low value of the excess molar enthalpy at infinite dilution, when compared with all the other solutes. The interaction of this compound with the ILs is highly influenced by the temperature.

Gas–Liquid Partition Coefficients. Gas–liquid partition coefficients, K_L , were calculated from retention times using the densities of the pure ILs previously reported.^{25,27,28} Assuming an ideal gas phase, the gas–liquid partition coefficients can be used to understand the terpenes and terpenoids extraction using ILs, and their subsequently evaporation in order to recover the ILs, at low pressures. Moreover, these parameters are also useful to understand the role of ILs on the fractionation of a complex mixture of terpenes and terpenoids. Results at a fixed temperature are presented in [Figure 4](#). In general, the highest

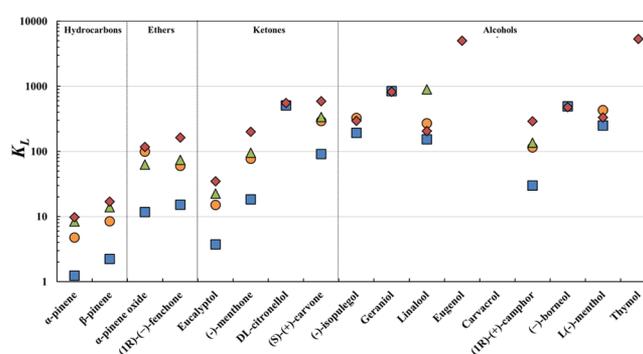


Figure 4. Experimental gas–liquid partition coefficients, K_L , for terpenes and terpenoids in the ILs studied, at 408.15 K. \square , $[\text{C}_4\text{mim}]\text{Cl}$; \circ , $[\text{C}_4\text{mim}][\text{CH}_3\text{SO}_3]$; Δ , $[\text{C}_4\text{mim}][(\text{CH}_3)_2\text{PO}_4]$; \diamond , $[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3]$.

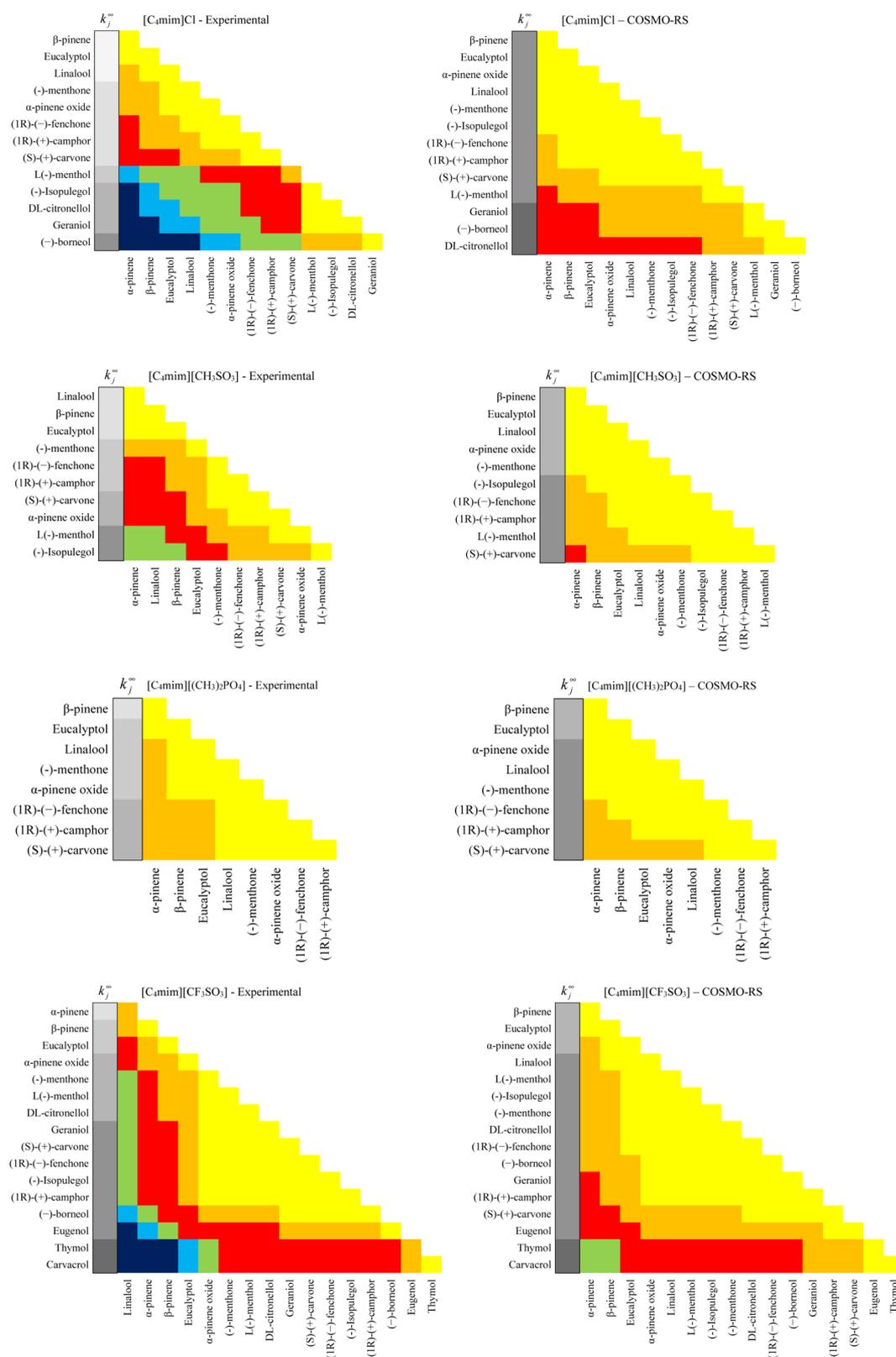


Figure 5. Experimental and COSMO-RS predictions of S_j^∞ and k_j^∞ of all solutes at 408.15 K in the different ionic liquids studied. Color code: yellow [1–2]; auburn [2–4]; red [4–10]; green [10–20]; blue [20–30]; and navy >30. Capacities, white <0.01; off-white [0.01–0.05]; light gray [0.05–0.1]; medium gray [0.1–0.2]; dark gray [0.2–1]; slate [1–2]; charcoal [2–5]; and black >5.

values are observed for more polar solutes like alcohols, with the less polar IL, $[C_4mim][CF_3SO_3]$. As expected, α - and β -pinene present the lowest values of the gas liquid partition coefficients, especially with the IL $[C_4mim]Cl$. These coefficients indicate the

possibility to separate terpenes from the terpenoid alcohol or ketone fractions. The K_L always decreases with increasing temperature as can be seen in Table S4 of the [Supporting Information](#).

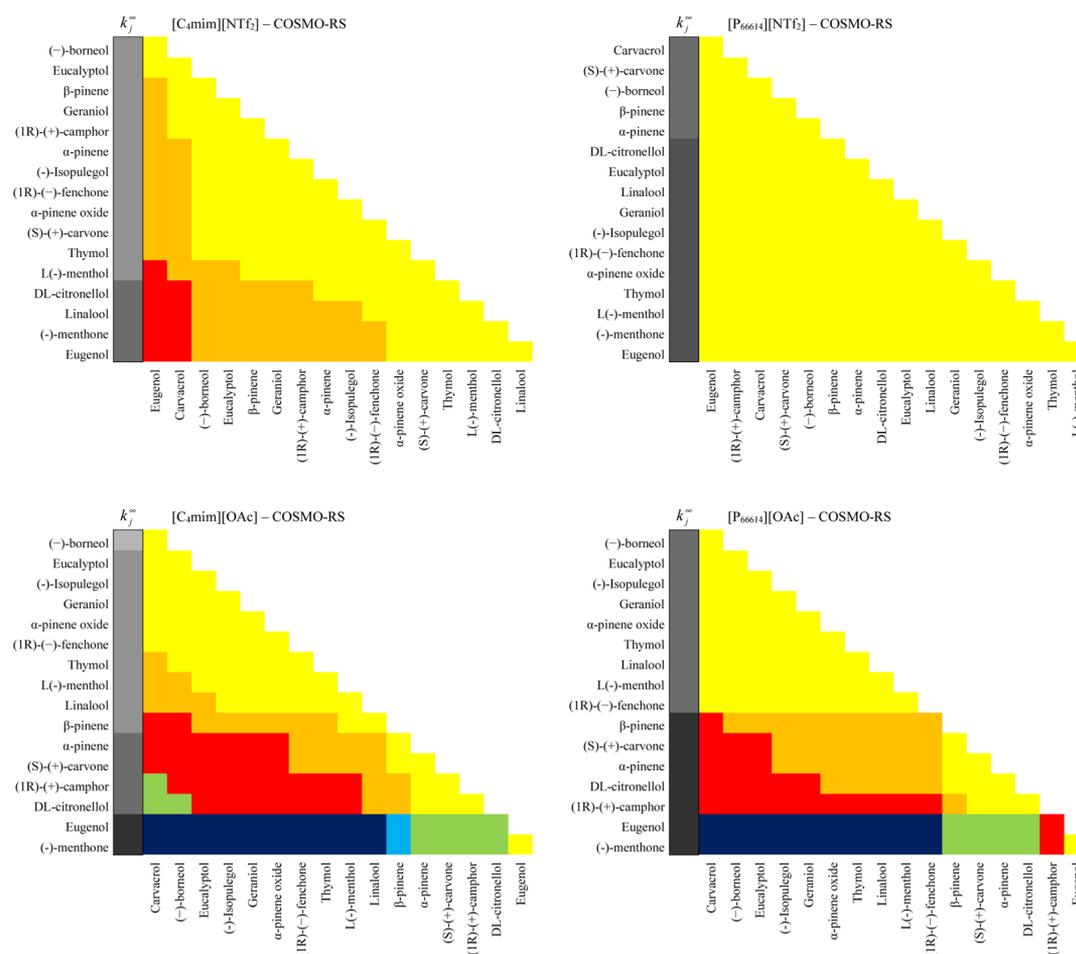


Figure 6. S_{ij}^{∞} and k_j^{∞} of all solutes at 408.15 K in selected ILs, computed by COSMO-RS. Color code: Selectivities, yellow [1–2]; auburn [2–4]; red [4–10]; green [10–20]; blue [20–30]; and navy >30; Capacities, white <0.01; off-white [0.01–0.05]; light gray [0.05–0.1]; medium gray [0.1–0.2]; dark gray [0.2–1]; slate [1–2]; charcoal [2–5]; and black >5.

Selectivities and Capacities. Selectivities, S_{ij}^{∞} , and capacities, k_j^{∞} , can be used to evaluate the ILs performance as solvents for separation processes.^{29–31} Taking into account the similarities in molecular structures and physical properties of terpenes and terpenoids, and therefore, the problems involved in their extraction from essential oils and subsequent fractionation, these two parameters must be known. According to the definition, a suitable solvent should present both a high selectivity and capacity for the components to be separated.³² Experimental results along with the selectivities and capacities predicted using COSMO-RS are schematically presented in Figure 5.

The experimental capacity takes the highest values for the pairs containing thymol or carvacrol, when the anion of the IL is $[\text{CF}_3\text{SO}_3]^-$ (1.661 and 1.671, respectively), and the lowest values for the pairs containing β -pinene or eucalyptol in $[\text{C}_4\text{mim}]\text{Cl}$ (0.005 and 0.006, respectively). From the experimental selectivities it is possible to identify the most complicated separation problems: (–)-menthone/ α -pinene oxide and thymol/carcacrol, with a S_{ij}^{∞} value close to 1 in the ILs $[\text{C}_4\text{mim}]\text{Cl}$ and $[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3]$, respectively. Inversely, the pairs linalool/thymol and linalool/carcacrol present high selectivity and capacity values with the IL $[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3]$, showing that this ionic liquid may be used in their separation. In general, experimental capacities are considerably lower than 1 and most of the selectivities fall in the range [1–2] and [2–4].

Selectivity ranges were chosen based on the numerical results obtained. Among the studied ILs, $[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3]$ is the one that seems to present high selectivities and capacities, indicating that ILs with low polarity should be used in the terpenes and terpenoids separation. However, the major limitation that the ionic liquids studied in this work present are the low capacities that would prevent their application into a separation process.

To improve the separation efficiency, new ILs must be evaluated. For that purpose, an ILs screening, computed using COSMO-RS, was attempted. To validate COSMO-RS predictions, the ILs studied in this work were used. Figure 5 shows that the selectivities obtained with COSMO-RS are generally lower than the experimental ones, which may be attributed to an overestimation of the hydrogen bonding interactions between ILs and solutes. Accordingly, COSMO-RS capacities are in general superior to the experimental ones. In spite of the quantitative deviations obtained with COSMO-RS from experimental data, in general the model is able to correctly estimate the order of the selectivities and capacities for the terpenes and terpenoids studied. A better agreement with the experimental data is obtained for the less polar ILs, such as $[\text{C}_4\text{mim}][(\text{CH}_3)_2\text{PO}_4]$ and $[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3]$.

According with the experimental results obtained in this work, better selectivities and capacities are achieved with the less-polar ILs. As the COSMO-RS predictions seem to be more precise also for these compounds, a set of selectivities and capacities of

Table 3. Selectivities (S_{ij}^{∞})/Capacities (k_j^{∞}) at Infinite Dilution for α -Pinene/ β -Pinene at 408.15 K in Different Solvents

solvent	selectivities (S_{ij}^{∞})/capacities (k_j^{∞})	reference
[C ₄ mim]Cl	1.386/0.005	this work
[C ₄ mim][CH ₃ SO ₃]	1.364/0.024	
[C ₄ mim][(CH ₃) ₂ PO ₄]	1.271/0.044	
[C ₄ mim][CF ₃ SO ₃]	1.327/0.053	
[C ₄ mim][CF ₃ SO ₃]-COSMO-RS	1.313/0.105	
[C ₄ mim][[(C ₈ H ₁₇) ₂ PO ₂]-COSMO-RS	1.315/2.467	
[P ₆₆₆₁₄][[(C ₈ H ₁₇) ₂ PO ₂]-COSMO-RS	1.205/6.237	
[C ₄ mim][OAc]-COSMO-RS	1.590/1.137	
[P ₆₆₆₁₄][OAc]-COSMO-RS	1.260/5.940	
dinonyl phthalate	1.260/1.156 ^a	36
amine 220	1.304/0.849 ^a	
tricresyl phosphate	1.113/0.643 ^a	
Carbowax 6000	1.346/6.601 ^a	
ethylene glycol phthalate	1.375/0.292 ^a	
Carbowax 1500	1.424/1.300 ^a	

^aExtrapolated value.

terpenes and terpenoids with selected ILs was computed using COSMO-RS: cations, 1-butyl-3-methyl-imidazolium, [C₄mim]⁺; and trihexyltetradecylphosphonium, [P₆₆₆₁₄]⁺; were combined with the anions tetracyanoborate, [BCN₄]⁻; bis-(trifluoromethylsulfonyl)imide, [NTf₂]⁻; bis(2,4,4-trimethylpentyl)phosphinate, [(C₈H₁₇)₂PO₂]⁻; tosylate, [TOS]⁻; methylsulfate, [CH₃SO₄]⁻; trifluoroacetate, [TFA]⁻; and acetate, [OAc]⁻. The ionic liquids were chosen based on the polarity of the cations and anions to cover a wide range of differentiated polarities between the ion pair. The most relevant cases unveiled by this search are presented in Figure 6, whereas the other compounds studied are presented in Figure S3 of the Supporting Information. COSMO-RS predictions show that the higher selectivities are obtained using polar anions such as bis(2,4,4-trimethylpentyl)phosphinate or acetate; whereas to obtain high capacities nonpolar cations such as phosphonium based must be preferred. This indicates that terpenes and terpenoids extraction must be made using cations and anions presenting distinct characteristics in order to fulfill simultaneously the requirements of high selectivities and capacities. The experimental validation of these predictions and the use of these ionic liquids for terpene and terpenoids separation are currently under development in our laboratory.

Among the compounds studied, a literature survey showed that an important separation problem is α -pinene/ β -pinene, a mixture extracted from turpentine,^{3,33} usually by steam-distillation.^{34,35} The experimental results obtained for S_{ij}^{∞} and k_j^{∞} are presented in Table 3, along with selected COSMO-RS results and values from literature for some other important solvents.

According to Table 3, it is possible to see that the experimental ILs studied present similar selectivities to the solvents studied by Díaz et al.³⁶ However, the capacities are much lower. As discussed before, to increase the capacity, ionic liquids with low polarity must be used. [C₄mim][CF₃SO₃] is the most promising solvent with respect to separation among the ILs experimentally evaluated in this work. On the basis of the COSMO-RS result for that IL, this is in agreement with the experimental information. Moreover, according to COSMO-RS, the ILs [P₆₆₆₁₄]-[(C₈H₁₇)₂PO₂] and [P₆₆₆₁₄][OAc] show good potential to be applied as agents for the α -pinene/ β -pinene separation.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.5b01357.

Pure terpenes and terpenoids data, detailed experimental procedure and theoretical foundations, infinite dilution activity coefficients and partial molar excess enthalpies, gas-liquid partition coefficients, σ -profiles, temperature dependence of the activity coefficients at infinite dilution, and selectivities and capacities (PDF).

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The paper was written through contributions of all authors. All authors have given approval to the final version of the paper.

Notes

The authors declare no competing financial interest.

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