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Deterpenation of Citrus Essential Oil by Liquid−Liquid Extraction with 1-Alkyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)amide Ionic Liquids

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ABSTRACT: Three 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ionic liquids, namely, those with ethyl-, hexyl-, or decyl- as the alkyl substituent chain, were evaluated as potential solvents for the deterpenation of citrus essential oil by liquid−liquid extraction. The citrus essential oil was simulated as a mixture of the terpene limonene and the oxyterpene linalool. The liquid−liquid equilibrium data for the ternary systems formed by limonene, linalool, and each of the ionic liquids selected were experimentally determined at 298.15 K. The suitability of the ionic liquids as solvents for the proposed process was evaluated by means of solute distribution ratio and selectivity values. The influence of the alkyl side chain in the imidazolium cation of the ionic liquids on the liquid−liquid equilibrium data was analyzed. By comparison with data previously reported in the literature for analogous systems, the influence of the ionic liquid anion on the proposed separation was also analyzed. The experimental data were satisfactorily correlated by means of both the nonrandom two-liquid (NRTL) and the universal quasichemical activity coefficient (UNIQUAC) thermodynamic models.

INTRODUCTION

Essential oils are volatile, aromatic oily liquids obtained from different parts of a plant (leaves, seeds, roots, fruits, etc.). The essential oil of a plant is mainly constituted by molecules with carbon, hydrogen, and oxygen atoms. Terpenes are the main class of compounds present;[1] however, they have a poor contribution to the flavor or aroma of the essential oil.[2] These compounds suffer hydrolysis reactions under heat and light conditions, and they are degraded generating undesirable compounds. Thus, the deterpenation of the essential oil results in a more stable product.[3] Oxygenated terpenes (or oxyterpenes) are present in a smaller percentage, but they are the compounds mainly responsible for most of the odor and flavor characteristics of the oil. They mostly consist of alcohols, aldehydes, and esters.[4] Currently, the most used processes to deterpenate the essential oils are vacuum distillation[5] and liquid−liquid extraction,[2,6,7] but new technologies are being developed in this emerging industry, such as membrane technologies[8] or supercritical extraction.[9]

The choice of solvent is the most critical aspect in the design of liquid−liquid extraction processes. The selection of a better solvent will result in an improved, more efficient process. Over the past decade, ionic liquids have generated growing interest in academia and industry as a potential alternative to conventional volatile organic solvents in reaction and separation processes.[10] Although it is hard to generalize any property for all of the members of the broad ionic liquid family (beyond their definition of salts that melt below 100 °C), they usually exhibit a negligible vapor pressure under normal operation conditions, they have good solvation ability, and their properties can be tuned by judicious choice of the constitutive ions.[11] Due to this interesting set of properties, ionic liquids have been largely explored in recent years as alternative solvents in liquid−liquid extraction processes.[12] Within the general effort of our research group in this area over the last years, a series of works were published on the potential use of ionic liquids for the deterpenation of citrus essential oil simulated as a mixture of its two main components: the terpene limonene and the oxyterpene linalool.[13−15] Specifically, the liquid−liquid equilibria of (limonene + linalool + ionic liquid) ternary systems were determined for the following ionic liquids: 1-ethyl-3-methylimidazolium methanesulfonate ($[C_2mim][OMs]$),[13] 1-ethyl-3-methylimidazolium ethylsulfate ($[C_2mim][EtSO_4]$),[14] and 1-ethyl-3-methylimidazolium 2-(2-methoxyethoxy)ethylsulfate ($[C_2mim][Me(OEt)_2SO_4]$).[15] The first two ionic liquids were investigated at 298.15 K, whereas for the latter a study of the influence of the temperature was carried out by determining the equilibrium data at T = (298.15, 308.15, and 318.15) K, obtaining the best results at 298.15 K.[15]

To get a deeper knowledge of the possibilities of ionic liquids as a solvent for the depertenation of citrus essential oil, three more ionic liquids are studied in this work. Namely, the homologous hydrophobic ionic liquids 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ($[C_2mim][NTf_2]$), 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ($[C_6mim][NTf_2]$), and 1-decyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ($[C_{10}mim][NTf_2]$) were chosen. Imidazolium ionic liquids with the $[NTf_2]^-$ anion exhibit very interesting thermophysical properties, such as very good thermal stability, relatively low viscosity, and low melting points.[16,17] The combined study of these three ionic liquids allows an analysis of the influence of the variation of the alkyl substituent chain in the imidazolium cation on the deterpenation. This is one of the most popular tunable structural features in ionic liquids, besides the own nature of the cation and the anion.[18] Moreover, the results

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Table 1. CAS Number, Experimental Water Content (w_{H_2O}), and Experimental and Literature Values for Density (ρ) and Refractive Index (n_D), at 298.15 K and Atmospheric Pressure, for Limonene, Linalool, and the [$C_n$mim][NTf_2] Ionic Liquids Used in the Present Work

		w_{H_2O} (ppm)	ρ (g·cm^{-3})		n_D	
compound	CAS no.	exp.	exp.	lit.	exp.	lit.
limonene	5989-27-5	152	0.83868	0.8383[23]	1.47081	1.4701[23]
linalool	78-70-6	204	0.85683	0.85760[24]	1.45961	1.4601[25]
[C_2mim][NTf_2]	174899-82-2	298	1.51891	1.51845[26]	1.42298	1.4230[26a]
[C_6mim][NTf_2]	382150-50-7	87	1.37209	1.37213[27]	1.42879	1.42958[27]
[C_{10}mim][NTf_2]	433337-23-6	76	1.27840	1.2780[28]	1.43584	1.4356[28]

[a] Interpolated value.

for [C_2mim][NTf_2] are directly comparable to the results obtained for the other ionic liquids with the [C_2mim]$^+$ cation in our previous works, providing a better insight of the influence of the nature of the anion.

Specifically, this work reports the liquid–liquid equilibria, at 298.15 K, for the ternary systems formed by limonene, linalool, and [$C_n$mim][NTf_2], where n stands for the number of carbons in the alkyl substituent chain of the cation and will take the values 2, 6, or 10. A correlation of the experimental liquid–liquid equilibrium is made by means of the nonrandom two-liquid (NRTL)[19] and universal quasichemical activity coefficient (UNIQUAC)[20] thermodynamic models.

EXPERIMENTAL SECTION

Materials. (R)-(+)-Limonene was supplied by Sigma-Aldrich, and (±)-linalool was purchased from SAFC. Their nominal purities were ω = 0.97 and $\omega \geq$ 0.97, respectively. Both chemicals were used without further purification.

The ionic liquids [$C_n$mim][NTf_2] were synthesized following an analogous procedure to that described elsewhere.[21] In a first step, 1-methylimidazole (Sigma-Aldrich, ω = 0.99) was alkylated with the corresponding haloalkane: bromoethane (Sigma-Aldrich, ω = 0.98), 1-chlorohexane (Fluka, $\omega \geq$ 0.99), or 1-chlorodecane (Fluka, $\omega \geq$ 0.97), at a temperature in the range T = (313.15 to 353.15) K (depending on the haloalkane) under inert atmosphere, for 48 h. The formed 1-alkyl-3-methylimidazolium halide was dissolved in acetonitrile (Panreac, ω > 0.999) and washed several times with ethyl acetate (Aldrich, $\omega \geq$ 0.995), to eliminate unreacted starting materials. After washing, most of the organic solvent was removed in a rotary evaporator, followed by stirring and heating at 343.15 K for 48 h under high vacuum (< 0.1 mbar) to complete the removal of any residual volatile compounds present. The chemical identity and purity of the intermediate halide ionic liquids obtained in this first step was verified by ^{1}H NMR and ^{13}C NMR spectroscopy.

In a second stage, the synthesized halide ionic liquids were dissolved in water and were contacted at ambient temperature with an aqueous solution of lithium bis(trifluoromethylsulfonyl)amide (Solvionic, $\omega \geq$ 0.99), with slight excess of the latter, to obtain the desired [$C_n$mim][NTf_2] ionic liquids via a metathetic reaction. Turbidity was observed instantaneously upon mixing of the aqueous solutions, as a result of the hydrophobicity of the formed ionic liquid, but the stirring of the medium was maintained for at least 4 h. Dichloromethane (Fluka, ω > 0.999) was added, dissolving the [$C_n$mim][NTf_2] in the organic phase, while the spectator ions remained in the aqueous phase. The organic phase was disengaged and washed several times with fresh water, ensuring that no precipitation was observed by addition of silver nitrate to the residual aqueous phase, thus indicating the absence of halide ions at significant levels.[22] The dichloromethane was removed by rotary evaporation, and elimination of residual volatile impurities was completed by connecting the ionic liquid to a high vacuum line (< 0.1 mbar), while stirring and heating at 343.15 K for no less than 48 h. The chemical structure of the desired ionic liquids was confirmed by ^{1}H NMR and ^{13}H NMR. Their water content (one of the most critical impurities in ionic liquids)[22] was measured by Karl Fischer titration with a MetrOhm 737 KF coulometer and found to be lower than 300 ppm in any case. The estimated minimum purity of the synthesized ionic liquids was ω > 0.995 for all of the products.

The CAS number and water content of the pure compounds used in this work are reported in Table 1. Their experimental densities and refractive indices at 298.15 K, respectively measured with an Anton Paar DMA 5000 densimeter (with an uncertainty in the measurements of $\pm\ 3 \cdot 10^{-5}$ g·cm^{-3}, and temperature controlled with an uncertainty of ± 0.01 K with a built-in thermometer) and an ATAGO RX-5000 refractometer (with an uncertainty in the measurements of $\pm\ 4 \cdot 10^{-5}$, and temperature controlled with an uncertainty of ± 0.02 K by means of a HeroTherm thermostat), are also shown and compared with available literature values published by other authors.[23–28]

Procedure. Mixtures of the three components (or just two, in the case of the binary tie-lines) of the systems (limonene + linalool + [$C_n$mim][NTf_2]), with global compositions within the immiscible region were prepared and placed inside jacketed liquid–liquid equilibrium glass cells. The temperature of the cell was kept constant by means of a Selecta Ultraterm 6000383 thermostatic bath, with an uncertainty of ± 0.02 K in the measurement of the temperature. The mixtures were vigorously stirred for at least 2 h and then allowed to settle for a minimum of 5 h. These times were found to be sufficient to ensure the achievement of the equilibrium and the complete separation of the phases, respectively. Previous tests showed that no composition variation was observed when increasing these times. Samples from each equilibrated phase were taken without disturbance of the interface and put inside tubes for NMR spectroscopy. Deuteriated methanol (Aldrich, 99.8+ atom % D) was used to dissolve the samples of the system (limonene + linalool + [C_2mim][NTf_2]), whereas deuteriated chloroform (Aldrich, 99.8 atom % D) was used for the samples of the other two systems. The NMR samples thus prepared were immediately sealed and stored for compositional analysis.

The compositions of the tie-line ends in the liquid–liquid equilibria of the (limonene + linalool + [$C_n$mim][NTf_2])

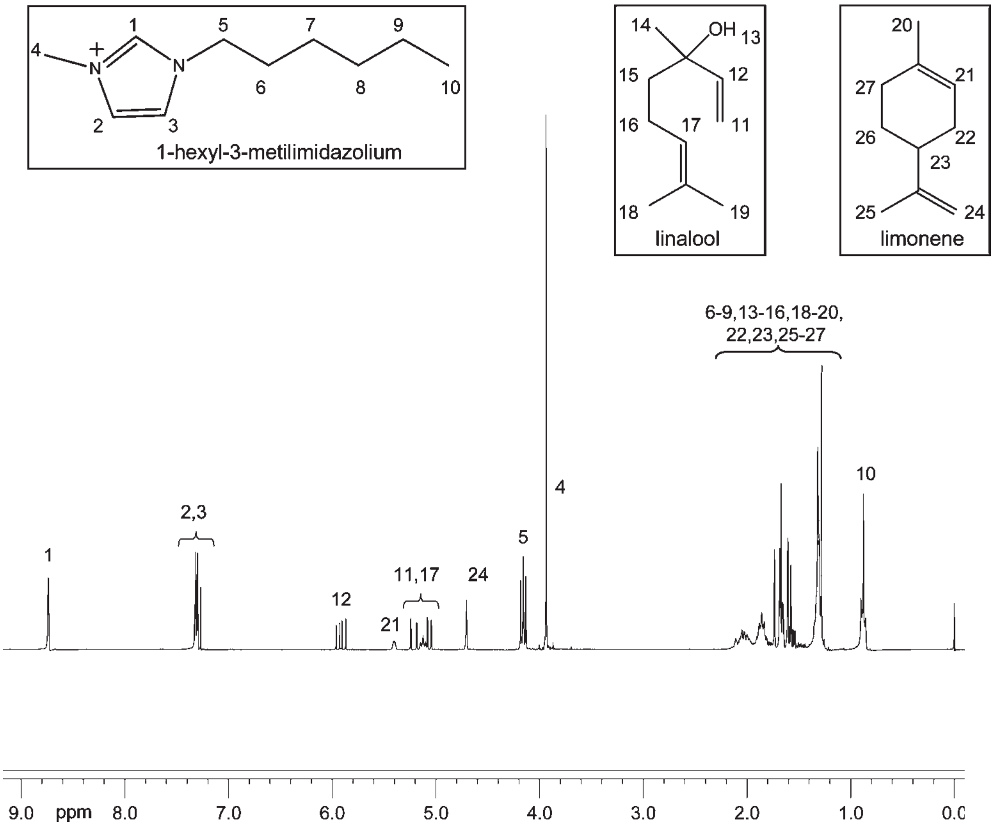

Figure 1. Example of ^{1}H NMR spectrum for a ternary mixture of (limonene + linalool + [$C_n$mim][NTf_2]) (in this particular case, [C_6mim][NTf_2]). The assignment of each peak to the hydrogen atoms in the chemical structures is shown. (Note: the anion of the ionic liquid is not drawn, since it does not have any hydrogen atom and therefore does not generate any peak in the spectrum.)

systems were determined by ^{1}H NMR spectroscopy. Several examples, by our group and others, of the satisfactory use of this technique for the compositional analysis of liquid−liquid equilibrium tie-lines in ternary systems involving ionic liquids, can be found in the literature.[13,14,18,29−31] All samples were run at 298.15 K in a 7.04 T Varian Mercury 300 spectrometer (300 MHz for ^{1}H resonance), with a relaxation time of 25 s, to ensure a good correspondence of the areas under the peaks in the spectra with the relative concentration of hydrogen atoms responsible for the generation of such peaks. The accuracy of the analytical technique was quantified by preparing homogeneous samples by weight (all weighing was carried out on a Mettler Toledo AT 261 balance with an uncertainty of $\pm 10^{-4}$ g), with a known composition lying in the vicinity of the immiscibility region and running them in the NMR spectrometer at the conditions described. All peaks were assigned to the protons in the chemical structures of the compounds involved (Figure 1), and different sets of peaks were selected. The minimum deviations between the actual and the calculated compositions were found when choosing the following peaks (see numbering in Figure 1): for the ionic liquid, peaks 4 and 5; for the linalool, peaks 12 and 11 to 17; and for the limonene, peaks 21 and 24. Since more than one peak was selected for each compound, pondered averages were carried out in each case to conclude a single value of area per molecule or ion, prior to calculating the molar fractions. For this optimized selection of peaks, the estimated uncertainty in the determination of the molar fraction compositions was ± 0.007 for the organic-rich (top) phases and ± 0.009 for the ionic liquid-rich (bottom) phases.

■ RESULTS AND DISCUSSION

Liquid−Liquid Equilibrium Data. The liquid−liquid equilibrium data for the ternary systems (limonene + linalool + [$C_n$mim][NTf_2]; with n = 2, 6, or 10), at 298.15 K, are reported in Table 2.

Figure 2 shows the equilateral triangular diagrams with the graphical representation of the liquid−liquid equilibrium data. All three systems correspond to Type II, according to the classification proposed by Treybal,[32] since they present two immiscible pairs (limonene−ionic liquid and linalool−ionic liquid), a completely miscible pair (limonene−linalool), and only one continuum immiscibility region. Linalool is more soluble than limonene in the three ionic liquids explored, likely due to the preferential interaction of its hydroxyl group with the aromaticity of the imidazolium ring.[33] It can be observed that the size of the immiscibility region decreases as the length of the alkyl substituent chain in [$C_n$mim][NTf_2] increases. It can be noted that the solubility of the ionic liquid in the top phase is very low or negligible. Also, the system with [C_{10}mim][NTf_2] clearly exhibits solutropy,[34] with the slopes of the tie-lines switching from positive to negative as the concentration of linalool in the system is increased, whereas this remains uncertain for the system with [C_6mim][NTf_2]. In any case, the solutrope for the latter case would be located at a very low concentration of linalool.

The suitability of each ionic liquid to extract the linalool from the essential oil mixture was evaluated from the experimental data at 298.15 K, by means of two classical parameters, namely

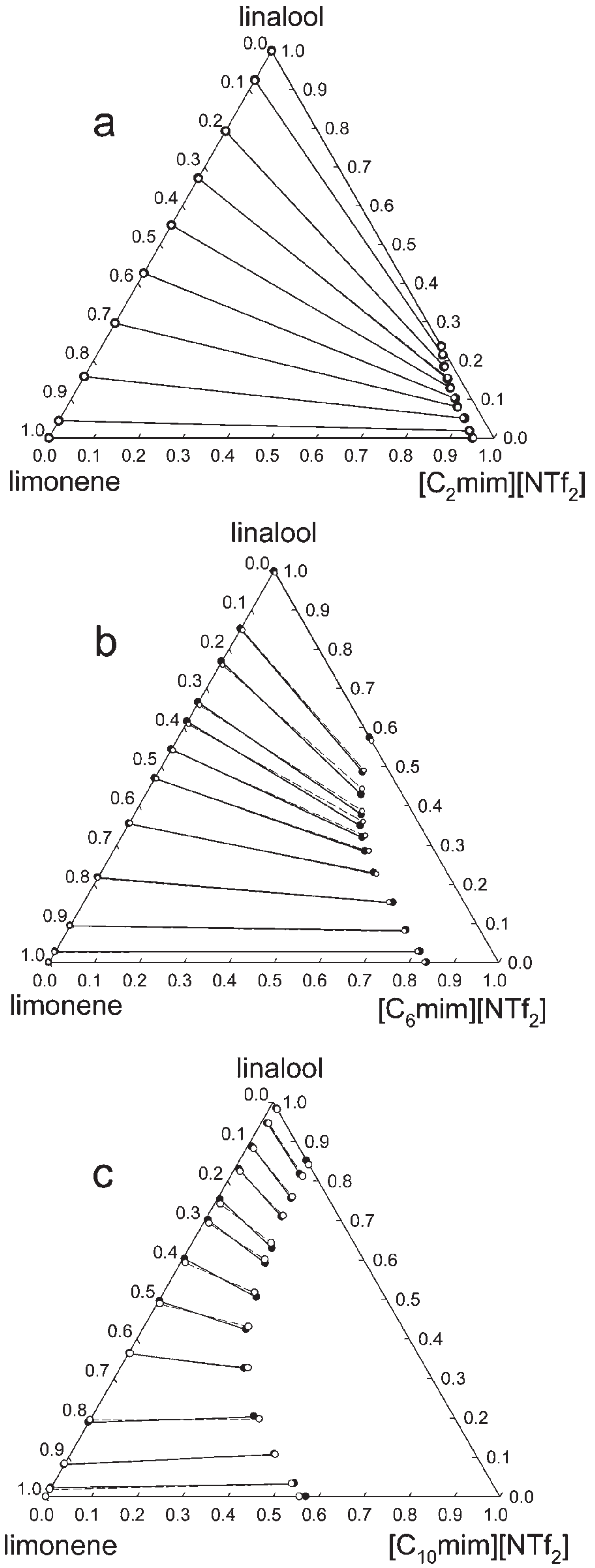

Figure 2. Experimental tie-lines (solid circles, solid lines) and their corresponding correlated tie-lines obtained with the UNIQUAC model with a previously fixed value of β_∞ (open circles, dashed lines), for the ternary systems (limonene + linalool + ionic liquid), at 298.15 K. Ionic liquid: (a) $[C_2mim][NTf_2]$; (b) $[C_6mim][NTf_2]$; (c) $[C_{10}mim][NTf_2]$.

Table 2. Composition of the Experimental Tie-Line Ends, Solute Distribution Ratio (β), and Selectivity (S) for the Ternary Systems (Limonene + Linalool + $[C_nmim][NTf_2]$) (with n = 2, 6, or 10), at 298.15 K[a]

ionic liquid-rich phase			organic-rich phase				
x_1	x_2	x_3	x_1	x_2	x_3	β	S
Limonene + Linalool + $[C_2mim][NTf_2]$							
0.049	0.000	0.951	1.000	0.000	0.000		
0.046	0.019	0.935	0.956	0.044	0.000	0.43	8.97
0.041	0.051	0.908	0.841	0.159	0.000	0.32	6.58
0.042	0.081	0.877	0.703	0.297	0.000	0.27	4.56
0.036	0.102	0.862	0.574	0.426	0.000	0.24	3.82
0.034	0.130	0.836	0.450	0.550	0.000	0.24	3.13
0.028	0.153	0.819	0.329	0.671	0.000	0.23	2.68
0.020	0.185	0.795	0.207	0.793	0.000	0.23	2.41
0.008	0.214	0.778	0.076	0.924	0.000	0.23	2.20
0.000	0.237	0.763	0.000	1.000	0.000	0.24	
Limonene + Linalool + $[C_6mim][NTf_2]$							
0.160	0.000	0.840	1.000	0.000	0.000		
0.161	0.028	0.811	0.972	0.028	0.000	1.00	6.04
0.165	0.082	0.753	0.906	0.094	0.000	0.87	4.79
0.158	0.153	0.689	0.782	0.218	0.000	0.70	3.47
0.163	0.229	0.608	0.645	0.355	0.000	0.65	2.55
0.155	0.284	0.561	0.530	0.470	0.000	0.60	2.07
0.143	0.320	0.537	0.456	0.544	0.000	0.59	1.88
0.133	0.349	0.518	0.385	0.615	0.000	0.57	1.64
0.116	0.377	0.507	0.336	0.664	0.000	0.57	1.64
0.091	0.428	0.481	0.232	0.768	0.000	0.56	1.42
0.059	0.486	0.455	0.148	0.852	0.000	0.57	1.43
0.000	0.573	0.427	0.000	0.998	0.002	0.57	
Limonene + Linalool + $[C_{10}mim][NTf_2]$							
0.427	0.000	0.573	1.000	0.000	0.000		
0.435	0.033	0.532	0.978	0.022	0.000	1.50	3.37
0.442	0.108	0.450	0.919	0.081	0.000	1.33	2.77
0.440	0.203	0.357	0.812	0.188	0.000	1.08	1.99
0.400	0.325	0.275	0.634	0.363	0.003	0.90	1.42
0.347	0.423	0.230	0.502	0.495	0.003	0.85	1.24
0.283	0.505	0.212	0.392	0.602	0.006	0.84	1.16
0.221	0.591	0.188	0.292	0.701	0.007	0.84	1.11
0.187	0.629	0.184	0.239	0.752	0.009	0.84	1.07
0.126	0.708	0.166	0.160	0.828	0.012	0.86	1.09
0.080	0.756	0.164	0.102	0.886	0.012	0.85	1.09
0.032	0.817	0.151	0.039	0.946	0.015	0.86	1.05
0.000	0.851	0.149	0.000	0.984	0.016	0.86	

[a] The molar fractions of limonene, linalool, and ionic liquid are represented by x_1, x_2, and x_3, respectively.

solute distribution ratio (β) and selectivity (S), defined as:

$$\beta = \frac{x_2^{\mathrm{II}}}{x_2^{\mathrm{I}}} \qquad (1)$$

$$S = \frac{x_2^{\mathrm{II}}}{x_2^{\mathrm{I}}} \cdot \frac{x_1^{\mathrm{I}}}{x_1^{\mathrm{II}}} \qquad (2)$$

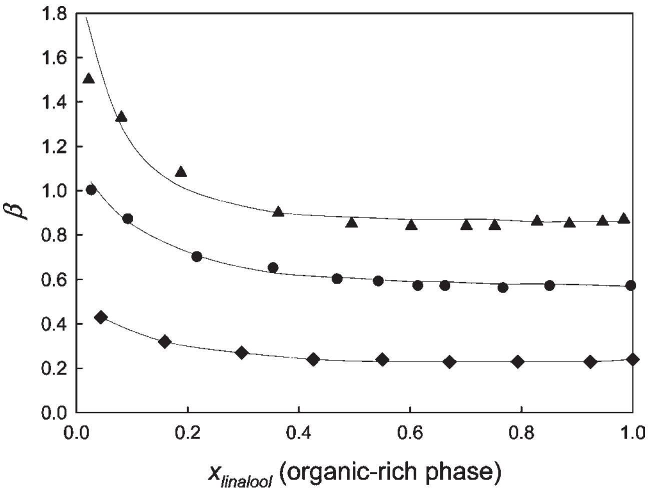

Figure 3. Experimental values of the solute distribution ratio (β), as a function of the molar fraction of linalool in the organic-rich phase (x_{linalool}) for the systems (limonene + linalool + $[C_2mim][NTf_2]$) (diamonds), (limonene + linalool + $[C_6mim][NTf_2]$) (circles), and (limonene + linalool + $[C_{10}mim][NTf_2]$) (triangles), at 298.15 K. The correlated values obtained with the UNIQUAC model fixing β_∞ are plotted as solid lines.

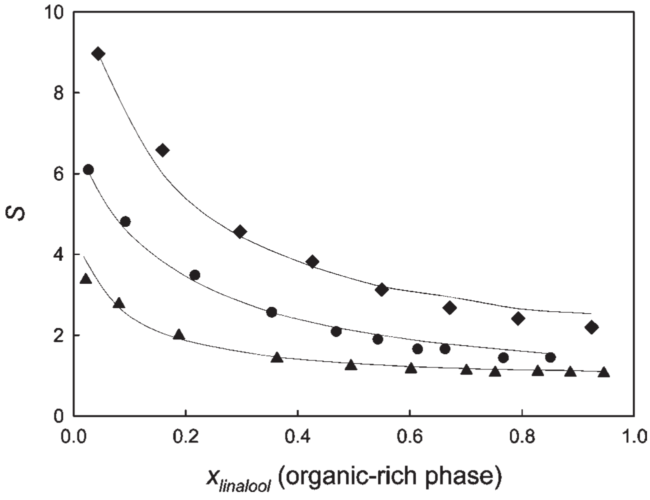

Figure 4. Experimental values of the selectivity (S), as a function of the molar fraction of linalool in the organic-rich phase (x_{linalool}) for the systems (limonene + linalool + $[C_2mim][NTf_2]$) (diamonds), (limonene + linalool + $[C_6mim][NTf_2]$) (circles), and (limonene + linalool + $[C_{10}mim][NTf_2]$) (triangles), at 298.15 K. The correlated values obtained with the UNIQUAC model fixing β_∞ are plotted as solid lines.

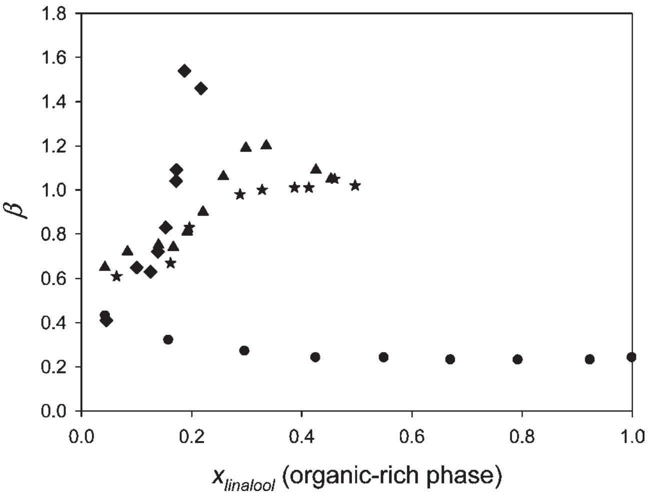

Figure 5. Solute distribution ratio (β), as a function of the molar fraction of linalool in the limonene-rich phase (x_{linalool}), for the systems (limonene + linalool + $[C_2mim][OMs]$)[13] (diamonds), (limonene + linalool + $[C_2mim][EtSO_4]$)[14] (triangles), (limoneno + linalool + $[C_2mim][NTf_2]$) (circles), and (limonene + linalool + $[C_2mim][Me(OEt)_2SO_4]$)[15] (stars), at 298.15 K.

where x stands for molar fraction, subscripts 1 and 2 represent the inert (limonene) and the solute (linalool), and superscripts I and II represent the organic-rich and ionic liquid-rich phases, respectively. The values of these two parameters for the systems studied are listed in Table 2, along with the corresponding liquid−liquid equilibrium data. In the case of the system with the ionic liquid $[C_{10}mim][NTf_2]$ it can be observed that the values of β change from values bigger than the unity to values lower than the unity, being consistent with the existence of a solutrope, as discussed above.

Solute distribution ratio and selectivity are plotted as a function of the linalool concentration in the organic-rich phase in Figures 3 and 4, respectively. Both parameters initially decrease, for all three systems, as the concentration of linalool increases, and then they plateau at higher linalool concentrations (with perhaps the only exception of selectivity for the system with $[C_2mim][NTf_2]$, which monotonically decreases over the whole composition range). For a given molar fraction of linalool in the top phase, the solute distribution ratio increases as the length of the alkyl substituent chain of the ionic liquid increases, whereas the selectivity follows the opposite trend. The trends observed can be explained on the basis of segregated domains in the ionic liquids. It is known that polar and nonpolar domains may exist in imidazolium ionic liquids with alkyl substituents.[35−37] The presence of nonpolar domains increases as the length of the alkyl substituents increases. Therefore, as n increases in the $[C_nmim][NTf_2]$ ionic liquids, the most hydrophobic limonene will find better accommodation in the larger nonpolar domains of the ionic liquid phase. Linalool will also partition more easily to the ionic liquid phase with larger hydrophobic domains, resulting in a greater solute distribution ratio, although the overall effect will be a reduction in selectivity. With an increasing presence of limonene and linalool in the extract, the two phases will get more similar in composition, causing a reduction in the difference of the interactions occurring within one phase and within the other one; thus, solute distribution ratio and selectivity vary to a minor extent when the global concentration of limonene and linalool in the system is high enough.

A higher value of β means that a smaller amount of solvent is needed to treat a given feed, but at the same time a lower value of S implies the need for a larger number of separation stages to achieve a specific degree of separation. Therefore, in addition to the compromise between the opposite trends in solute distribution ratio and selectivity, other aspects may be considered in selecting the best ionic liquid among those tested. To address this issue, it may be worth noting that no ionic liquid was detected in the top phase of the system with $[C_2mim][NTf_2]$, at any concentration in the system. This would be an advantageous aspect, since it might avoid the need for recovery of the solvent from the raffinate stream in a real continuous process.

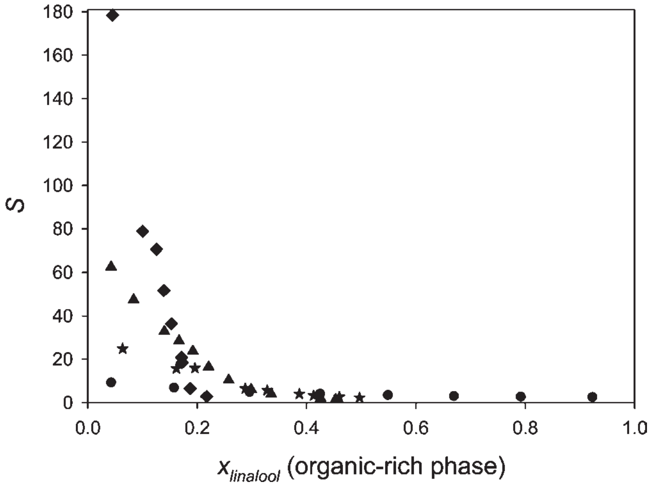

Figure 6. Selectivity (S), as a function of the molar fraction of linalool in the limonene-rich phase (x_{linalool}), for the systems (limonene + linalool + [C_2mim][OMs])[13] (diamonds), (limonene + linalool + [C_2mim][$EtSO_4$])[14] (triangles), (limoneno + linalool + [C_2mim][NTf_2]) (circles), and (limonene + linalool + [C_2mim][Me(OEt)$_2SO_4$])[15] (stars), at 298.15 K.

Nonetheless, it must be taken into account that some ionic liquid may enter the top phase, below the detection limit of the experimental technique used,[30] resulting in a critical loss of solvent if it is not recovered. Experiments in a pilot plant, prior to scale-up of the process, should pay particular attention to this issue. Further advantages associated with the ionic liquid with shorter alkyl side chain, compared to the other two ionic liquids, would also be lower viscosity[38] and lower price.

Since there are liquid−liquid equilibrium data available in the literature for other ionic liquids with the 1-ethyl-3-methylimidazolium cation to separate linalool from its mixtures with limonene,[13−15] a direct comparison of the effect of the anion is possible with the data reported herein for the system with [C_2mim][NTf_2]. Namely, the anions previously studied were methanesulfonate ([OMs]$^-$),[13] ethylsulfate ([$EtSO_4$]$^-$),[14] and 2-(2-methoxyethoxy)ethylsulfate ([Me(OEt)$_2SO_4$]$^-$).[15] Figures 5 and 6 show a comparison of β and S, at 298.15 K, for the different systems (limonene + linalool + [C_2mim][X]), with [X]$^-$ being one of the enumerated anions. There is no evident pattern for the evolution of the β values, with most series increasing as the concentration of linalool in the system increases, and the one of the [NTf_2]-based ionic liquid slightly decreasing. The ionic liquids with the sulfate-derived anions exhibit the highest values when low amounts of linalool are present in the system, but if the presence of linalool is more significant, then [C_2mim][OMs] shows the highest β values. It seems clear that the ionic liquid with the [NTf_2]$^-$ anion leads to the lowest values. Regarding the selectivity, the lowest values are also provided by [C_2mim][NTf_2], at least at low concentrations of linalool in the system. In this range of solute concentration, the highest values of S correspond to the system with [C_2mim][OMs], followed by [C_2mim][$EtSO_4$] and by [C_2mim][Me(OEt)$_2SO_4$]. At higher concentrations of linalool, the selectivities for the different series decrease and tend to converge. Taking into account that [C_2mim][OMs] is supercooled at 298.15 K and atmospheric pressure,[39] with the implicit risk of crystallization at some point in the process, it may be better to mark the [C_2mim][$EtSO_4$] as the preferable ionic liquid to carry out the targeted separation. At this point, the reasons behind this different behavior among anions remain unclear. Computational simulations for the studied systems may be helpful in understanding the relevant interactions in the systems, thus being useful in the optimized design of better ionic liquids to perform the desired separation of limonene and linalool.

Table 3. Structural Parameters r and q (UNIQUAC Model) of the Compounds Involved in the Ternary Systems Limonene + Linalool + [$C_n$mim][NTf_2]

compound	r	q	ref
limonene	6.2783	5.2080	36
linalool	7.0356	6.0600	36
[C_2mim][NTf_2]	9.8900	8.7800	41
[C_6mim][NTf_2]	12.970	10.920	41
[C_{10}mim][NTf_2]	15.6718	12.356	41, 42

Correlation. The novel liquid−liquid equilibrium data reported in this work were correlated by means of the widely used NRTL[19] and UNIQUAC[20] models. In the case of the NRTL model, the value of the nonrandomness parameter, α, was previously given the values 0.1, 0.2, and 0.3, in all cases. The structural parameters for the UNIQUAC model, r and q, were calculated from group contribution data,[40−42] and are shown in Table 3. A program by Sørensen and Arlt[43] was used, which allows the calculation of the binary interaction parameters for both models. This program uses two objective functions: first a function of activities, F_a, which does not require any previous knowledge of parameters; and then a function of compositions, F_b, which takes the parameters resulting from the convergence in F_a as initial guess to fit the experimental concentrations. The expression of these two objective functions is:

$$F_a = \sum_k \sum_i [(a_{ik}^{I} - a_{ik}^{II})/(a_{ik}^{I} + a_{ik}^{II})]^2 + Q \sum_n P_n^2 \qquad (3)$$

$$F_b = \sum_k \min \sum_i \sum_j (x_{ijk} - \hat{x}_{ijk})^2 + Q \sum_n {P_n}^2 + \left[\ln \left(\frac{\hat{\gamma}_{S\infty}^{I}}{\hat{\gamma}_{S\infty}^{II}} \beta_\infty \right) \right]^2 \qquad (4)$$

where a is the activity, x is the experimental molar fraction, "min" refers to a minimum obtained by the Nelder−Mead method, $\gamma_{S\infty}$ represents the solute activity coefficient at infinite dilution, and the symbol ^ on top of a variable indicates that it is a calculated value. Superscripts I and II refer to the phases in equilibrium, and subscripts i, j, and k to the components, the phases, and the tie-lines, respectively. Both functions include a penalization term (second term on the right-hand side of the equations) to reduce the risk of multiple solutions associated with large value parameters. In this penalization term, Q is an empirical constant, which was given Sørensen's recommended values of 10^{-6} in eq 3 and 10^{-10} in eq 4,[43] and P_n are the adjustable parameters (binary interaction parameters of the correlation model). F_b also includes a term that will only be relevant if a fixed value for the solute molar distribution ratio at infinite dilution, β_∞, is previously defined by the user. If this parameter is not fixed, then the last term in eq 4 will be zero.

The quality of the correlations was measured by means of the residual function F and by the mean error of the solute

Table 4. Residual Function, F, and Mean Error of the Solute Distribution Ratio, $\Delta\beta$, for the Correlation of the Experimental Liquid−Liquid Equilibrium Data of the Ternary Systems (Limonene + Linalool + $[C_n mim][NTf_2]$) (with n = 2, 6, or 10), at 298.15 K, with the NRTL and UNIQUAC Models, Fixing and without Fixing a Priori the Solute Distribution Ratio at Infinite Dilution, β_∞

ionic liquid	model	β_∞	F	$\Delta\beta$
$[C_2mim][NTf_2]$	NRTL (α = 0.2)		0.2467	10.6
		0.50	0.3058	1.9
	UNIQUAC		0.1450	1.9
		0.50	0.1460	1.4
$[C_6mim][NTf_2]$	NRTL (α = 0.2)		0.6896	3.0
		1.10	0.6918	2.4
	UNIQUAC		0.6045	6.9
		1.12	0.5586	2.6
$[C_{10}mim][NTf_2]$	NRTL (α = 0.3)		0.7465	3.4
		1.75	0.7465	3.5
	UNIQUAC		0.4827	25.2
		2.00	0.6338	6.2

Table 5. Binary Interaction Parameters (Δu_{ij}, Δu_{ji}) for the Correlation of the Experimental Liquid−Liquid Equilibrium Data of the Ternary Systems (Limonene (1) + Linalool (2) + $[C_n mim][NTf_2]$ (3)) at 298.15 K, by Means of the UNIQUAC Model and Previously Fixing a Value for β_∞

			Δu_{ij}	Δu_{ji}
ionic liquid	model	components	$J \cdot mol^{-1}$	$J \cdot mol^{-1}$
$[C_2mim][NTf_2]$	UNIQUAC,	1−2	1791.9	−1131.8
	β_∞ = 0.50	1−3	3821.1	−428.54
		2−3	3171.5	−1087.9
$[C_6mim][NTf_2]$	UNIQUAC,	1−2	1782.5	−1177.3
	β_∞ = 1.12	1−3	2703.9	−614.30
		2−3	2811.3	−1313.5
$[C_{10}mim][NTf_2]$	UNIQUAC,	1−2	2793.3	−1771.6
	β_∞ = 2.00	1−3	4419.3	−1567.1
		2−3	3088.2	−1686.5

distribution ratio, $\Delta\beta$, defined as:

$$F = 100\left[\sum_k \min \sum_i \sum_j \frac{(x_{ijk} - \hat{x}_{ijk})^2}{6M}\right]^{0.5} \tag{5}$$

$$\Delta\beta = 100\left[\sum_k \frac{(\beta_k - \hat{\beta}_k)/\beta_k}{M}\right]^{0.5} \tag{6}$$

where M is the total number of tie-lines, and all other variables and symbols have already been defined.

Two different ways were used to correlate the experimental data, in a similar manner to the procedure described by Sørensen and Arlt.[43] First, the correlation was performed without fixing a previous value for β_∞. After that, an optimal value of this parameter, found by trial and error, and considering the minimization of $\Delta\beta$ as the optimality criterion, was specified before carrying out the correlation. The values of F and $\Delta\beta$ for the NRTL (showing only the results with the α value leading to the best correlation out of the three values tried) and UNIQUAC models, both fixing and without fixing a previous value of β_∞, are shown in Table 4. The corresponding binary interaction parameters are shown in Table 5 for the UNIQUAC model fixing a previous value of β_∞, which turns out to be the model that better fits the experimental data. Figure 2 shows a comparison of experimental tie-lines and the corresponding correlated tie-lines calculated with the UNIQUAC model fixing a value of β_∞, for all three systems (limonene + linalool + $[C_n mim][NTf_2]$) studied. A simple visual inspection of the triangular diagrams confirms the good match between the experimental and correlated sets of tie-lines, and the suitability of the proposed model to correlate the liquid−liquid equilibrium data of the investigated systems. The accurate correlation of the experimental data is important to facilitate their computerized treatment, for instance, in process simulation software.

■ CONCLUSIONS

The liquid−liquid equilibrium data for the ternary systems (limonene + linalool + ($[C_2mim][NTf_2]$ or $[C_6mim][NTf_2]$ or $[C_{10}mim][NTf_2]$)) were experimentally determined at 298.15 K. Solute distribution ratios and selectivities calculated from the experimental data indicate that, in principle, the $[C_n mim][NTf_2]$ ionic liquids proposed can be used as extracting solvents for the deterpenation of citrus essential oil. The use of an ionic liquid instead of a conventional volatile solvent might offer inherent advantages, for example in the recovery of the solvent from the extract, as a result of the unvolatility of the ionic liquids.

The novel liquid−liquid equilibria investigated in this work permitted, for the first time, an analysis of the influence of the length of the alkyl side chain of the ionic liquid cation in the extraction of linalool from its mixtures with limonene. This is one of the main tunable structural features of ionic liquids for their customization for a particular application. The results, in terms of solute distribution ratio and selectivity, are undesirable: while the solute distribution ratio increases as the length of the alkyl side chain increases, the selectivity notably decreases. Other factors beyond those exclusively derived from the liquid−liquid equilibrium data should be considered prior to deciding the optimum alkyl chain length. For instance, their toxicity, biodegradability, or suitable thermophysical properties could be complementary evaluated.

However, the values of the solute distribution ratio and selectivity for $[C_n mim][NTf_2]$ were not as favorable as for other ionic liquids previously studied in the literature for the same purpose. A comprehensive comparison of all data available for ionic liquids as potential solvents for deterpenation of citrus essential oil by liquid−liquid extraction showed that $[C_2mim]$-$[OMs]$ or $[C_2mim][EtSO_4]$ were leading to the most promising results. To take advantage of the opportunity to "design" specific ionic liquids for a specific separation, it is necessary to continue studies of the type started here, on the influence of the cation an anion type, the substituent, and so forth. Ultimately, an optimal ionic liquid for the deterpenation of the citrus essential oil will be found.

The experimental liquid−liquid equilibrium data reported herein were satisfactorily correlated by means of both the NRTL and the UNIQUAC models, and the corresponding sets of binary interaction parameters were determined. Best results were obtained with the UNIQUAC model, especially when defining a priori a value of the solute distribution ratio at infinite dilution.

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