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# Essential Oil Terpenless by Extraction Using Organic Solvents or Ionic Liquids

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*Ionic liquids are gaining attention as potential substitutes for classic organic solvents in many different applications, especially as reaction media and separation agents. Search for an effective method for essential oils terpenless is necessary. Organic solvents are volatile substances, which contribute to environmental pollution and lead to important operating costs due to losses by evaporation. Thus, use of a* green-solvent *would avoid those difficulties. In this work, the possibility of using two organic solvents and an ionic liquid to carry out the citrus essential oil deterpenation is studied and the obtained results are compared. Citrus essential oil is simulated as a mixture of limonene and linalool; the solvents studied are 2-butene-1,4-diol, ethylene glycol, and the 1-ethyl-3-methylimidazolium methanesulfonate ionic liquid; and LLE data for the three ternary systems are reported. Data correlation is done by means of the NRTL equation. Solvent selection is studied by means of the solute distribution ratio and the selectivity, and compared to other solvents from the literature. The ionic liquid presents the highest selectivity, but close to other organic solvents, and results for solute distribution ratio depend on concentration range of extraction. Extraction process simulations using these solvents are carried out and the results are shown for comparison. Despite the fact that the ionic liquid does not get the highest linalool recovery, it provides the highest purity.* © 2006 American Institute of Chemical Engineers *AIChE J,* 52: 2089–2097, 2006
*Keywords: essential oils, ionic liquids, LLE, solvent extraction*

## Introduction

Room-temperature ionic liquids (RTILs) are defined as ionic compounds with low melting temperatures (below 100°C) with unique physical and chemical properties. Among them, it is usual to highlight their negligible vapor pressure, thermal and chemical stability, wide liquid range, or no flammability. Moreover, there is the possibility to "design" the best RTIL for a given application by careful selection of the anion and cation. This fact expands the amount of possible RTILs up to $10^{18}$. In recent years, RTILs have been getting increasing attention. Several ACS meetings,[1-4] journal special issues,[5] reviews,[6,7] and books[8] have collected incipient research performed on and about RTILs. More important, industrial applications of RTIL are now finally coming to light, demonstrating the interest of these new chemicals and encouraging further research.

Research on RTILs covers different fields. As they are a new class of liquids entirely composed of ions, all the chemistry that is performed on the usual molecular solvents needs to be investigated on these compounds. They are good solvents for many different substances, both organic and inorganic; thus, they are being investigated as reaction media,[1-6,8] solvents for separation purposes,[9-12] electrolytes,[9,13,14] and thermal fluids.[2,8] RTILs' negligible vapor pressure favors their separation from most mixtures; thus, application as entrainers for azeotropic

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and extractive distillations or as solvents for liquid extraction are of highest interest.[10,11]

Essential oils are responsible for the characteristic taste and odor of natural plants. Because of it, they are used in the food and cosmetics industries. The oil is composed by one or more terpenes and some oxygenated derivatives.[15] Nevertheless, the oxygenated compounds usually have better organoleptic properties. Nowadays, preparation of essential oils with a high content on oxygenated terpenoids presents some difficulties, due to their delicate characteristics. For this reason, a new process avoiding such difficulties would be very useful. Heat application can affect the organoleptic properties of the essential oil; thus, liquid extraction would be preferred rather than distillation.

In recent years, our research group has been working on phase equilibria applied to citrus essential oil deterpenation using different organic solvents.[16-20] To continue in search of an adequate solvent, in this work we analyze two new compounds: 2-butene-1,4-diol (BDO) and ethylene glycol (EG). Moreover, in cutting-edge research, the possibility of using an RTIL, 1-ethyl-3-methylimidazolium methanesulfonate ([emim][OMs], to improve results obtained at the moment is evaluated.

We simulate citrus essential oil as the mixture of its two main components, limonene and linalool, and then liquid-liquid equilibria of the different ternary systems formed with solvents are studied. The equilibrium data are correlated using the NRTL equation,[21] and the solvents' capacity to separate the mixture is evaluated by means of thermodynamic parameters: solute distribution ratios and selectivities. The solvents' comparison is extended to other organic compounds previously studied.[16-18] Finally, a simulation of the extraction column is performed using the HYSYS© software (AspenTech™) and the LLE experimental data reported here or from the literature. The number of equilibrium stages and the solvent-to-feed ratio are varied to study the extraction capacity of the different solvents and the linalool composition in the extracted product.

## Experimental Procedures

### *Reagents*

All chemicals were supplied by Fluka except the RTIL. R(+)-limonene (Lim), (±)-linalool (LiOH), and 2-butene-1,4-diol (BDO) were of *purum* grade and >98, >97, and >98 mass% nominal purities, respectively. Ethylene glycol (EG) was of *puriss.* grade and >99.5 mass% nominal purity. 1-Ethyl-3-methylimidazolium methanesulfonate ([emim][OMs]) was synthesized in the laboratory.

Densities and refractive indices of the pure components were measured experimentally. Results are shown in Table 1 and compared with values published in the literature. Densities were measured with an Anton Paar DMA 60/602 densimeter precise to within $\pm 10^{-2}$ kg·m$^{-3}$. Density of [emim][OMs] was measured on an Anton Paar DSA 48 precise to within $\pm 10^{-1}$ kg·m$^{-3}$. Refractive indices were measured with an Atago RX-5000 refractometer with an accuracy of $\pm 4 \cdot 10^{-5}$.

**Table 1. Density and Refraction Indices of the Pure Components**

| | $\rho$ (g · cm$^{-3}$) | | $n_D$ | |
|---|---|---|---|---|
| Component | exp. | lit. | exp. | lit. |
| R-(+)-Limonene | 0.83729 | 0.8383[22] | 1.47029 | 1.4701[22] |
| (±)-Linalool | 0.85746 | 0.85760[23] | 1.45956 | — |
| [emim][OMs] | 1.24373 | — | 1.49549 | — |
| Ethylene glycol | 1.10996 | 1.1100[22] | 1.43037 | 1.4306[22] |
| 2-Butene-1,4-diol* | 1.06931 | — | 1.47711 | — |
| *cis*-2-Butene-1,4-diol | | 1.06995[24] | | 1.4716[24] |
| *trans*-2-Butene-1,4-diol | | 1.06539[24] | | — |

Experimental and literature data at 298.15 K.
*~(1:1) mixture of *cis* and *trans* isomers.

### *Synthesis of 1-ethyl-3-methylimidazolium methanesulfonate*

The [emim][OMs] was obtained using a solvent-free, direct-synthesis method.[25,26] The stoichiometric quantity of methylimidazole (Aldrich, >99 mass%) was added dropwise to ethylmethanesulfonate (Fluka, >98 mass%) in a round-bottomed flask at ambient temperature. Then the flask was placed in a silicon oil bath at 60°C with a reflux condenser, with helium atmosphere, and agitated for one h. Remaining initial reagents were eliminated on a rotaevaporator at 50°C for 30 min, and the 1-ethyl-3-methylimidazolium methanesulfonate obtained was decolorized using activated carbon at 353.15 K for 2.5 h, again using agitation, the reflux condenser, and helium atmosphere. Then it was filtered and dried first on the rotaevaporator (50°C, 30 min) and then overnight under high vacuum, 90°C and agitation. $^1$H- and $^{13}$C-NMR were obtained to check that the compound was 1-ethyl-3-methylimidazolium methanesulfonate. Water content was measured with a Metrohm 737KF coulometer, using Hydranal (supplied by Riedel-de Haën) as titrating reagent, resulting in 157 ppm. and the physical properties were measured experimentally. Density and refractive index are shown in Table 1.

### *Procedure*

LLE data for the limonene + linalool + (2-butene-1,4-diol or ethylene glycol) were obtained by the analysis method using gas chromatography, which is the usual procedure. The procedure is explained in detail elsewhere.[27] Briefly, samples with compositions lying in the immiscible region were agitated for at least 1 h to get a good contact between both phases, and allowed to stand for at least 4 h. Equilibrium cells for the samples are jacketed and water from a bath thermostat (Selecta Ultraterm 6000383) was circulated to control the temperature to within ±0.1 K using a Testo 925 thermometer. Then samples of both layers were withdrawn using syringes and analyzed by gas chromatography. The gas chromatograph used was an HP 6890GC series equipped with a thermal conductivity detector and an HP5 capillary column (30m × 0.32mm × 0.25 $\mu$m). Helium was used as the mobile phase and injection volume was 0.5 $\mu$l with a split ratio of 1:100. Separation was made at 398.15 K under isothermal conditions. Calibration of the gas chromatograph was previously done using a pseudo-internal standard method, as the major component of the mixture (limonene in the limonene-rich samples, 2-butene-1,4-diol or ethylene glycol in the solvent-rich samples) was used as standard. The binodal curves were estimated using the cloud-

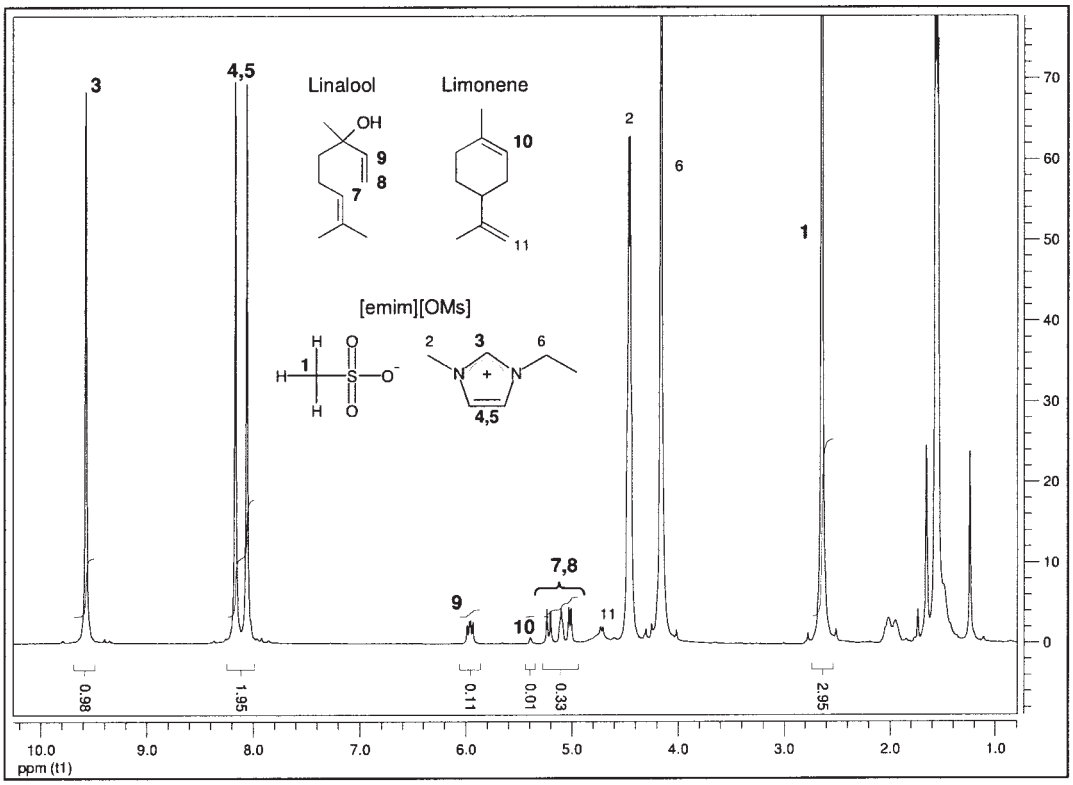


**Figure 1. Example of a $^1$H-NMR spectrum for a ternary mixture, with chemical structures and peaks identification.**

Peaks in bold were integrated for analysis.

point method, and then samples of known composition lying in the homogeneous region, but close to the binodal curve, were prepared by weight and analyzed on the gas chromatograph. The calibration function was established by fitting compositions as a function of the peaks' areas. The calibration was checked preparing a few samples of known composition, which were also analyzed on the gas chromatograph. The biggest errors on compositions were $\pm 0.003$ molar fraction in the limonene-rich phases and $\pm 0.004$ molar fraction in the solvent-rich phases.

For the limonene + linalool + 1-ethyl-3-methylimidazolium methanesulfonate system, composition analysis could not be obtained by gas chromatography. Thus, in order to keep our methodology, $^1$H-NMR spectroscopy was used to analyze the samples of each phase.[11] In this case, samples with the three components lying in the immiscible region were agitated for at least 1.5 h to get a good contact between both phases, and allowed to stand for at least 8 h (overnight). Experimental equipment is the same as that used with organic solvents, but samples withdrawn were analyzed by $^1$H-NMR spectroscopy using a Bruker DRX500 (11.74 T, 500 MHz). Sampling was done in screw-cap Wilmad tubes (Royal Imperial grade), with PTFE/silicone septa to avoid losses by vaporization. Deuterated solvent used was benzene (Aldrich, 99.95 atom% D), selected for its suitable peak. Benzene was not mixed with the sample, but added inside a sealed, capillary tube to the NMR tube. Prior to LLE data determination, errors of the analytical technique were measured in a similar way as before: samples of known composition were prepared by weight and then analyzed by $^1$H-NMR. The biggest errors obtained were $\pm 0.005$ in molar fraction. Figure 1 shows a $^1$H-NMR spectrum of the ternary mixture together with the reagents' chemical structure and selected peaks for integration and composition determination.

## Results and Data Correlation

Tables 2, 3, and 4 show the experimental LLE data for the systems limonene + linalool + 2-butene-1,4-diol or ethylene glycol or 1-ethyl-3-methyl imidazolium methanesulfonate. Experimental data were obtained at 298.15, 308.15, and 318.15 K for the systems with organic solvents in order to study the temperature effect. The system with the RTIL was investigated at 298.15 K only. Experimental data are shown in Figures 2, 3, and 4. It can be seen that (limonene + solvent) mutual solubility is very low, but linalool solubilizes the system (there is only one phase over 40 mol% linalool). Both organic solvents have tie-lines' slopes lying down towards the solvent's apex, but the ionic liquid has a change in the slope, an effect known as solutropy.

Data correlation was performed using the NRTL (Non-Random Two-Liquids) equation.[21] Despite the fact that it was originally intended for non-electrolytes, it has proved to be useful also in systems containing RTILs.[11,28,29] The nonrandomness parameter of NRTL, $\alpha$, was fixed to 0.1, 0.2, and 0.3, and the best result was used subsequently. The binary interaction parameters for the NRTL equation were obtained using a computer program described by S$\phi$rensen and Arlt,[30] which uses two objective functions. First, $F_a$, which does not require any previous guess for parameters, and after convergence the

**Table 2. Experimental Tie-Lines of the System Lim (1) + LiOH (2) + BDO (3)**

| BDO-Rich Phase | | | Limonene-Rich Phase | | |
|---|---|---|---|---|---|
| $x_1$ | $x_2$ | $x_3$ | $x_1$ | $x_2$ | $x_3$ |
| | | $T$ = 298.15 K | | | |
| 0.0100 | 0.0000 | 0.9900 | 0.9904 | 0.0000 | 0.0096 |
| 0.0138 | 0.0444 | 0.9418 | 0.9127 | 0.0782 | 0.0091 |
| 0.0167 | 0.0744 | 0.9089 | 0.8233 | 0.1533 | 0.0234 |
| 0.0253 | 0.1026 | 0.8721 | 0.7372 | 0.2154 | 0.0474 |
| 0.0318 | 0.1251 | 0.8431 | 0.6599 | 0.2644 | 0.0757 |
| 0.0430 | 0.1577 | 0.7993 | 0.5652 | 0.3097 | 0.1251 |
| 0.0573 | 0.1813 | 0.7614 | 0.4850 | 0.3332 | 0.1818 |
| 0.0669 | 0.1960 | 0.7371 | 0.4556 | 0.3429 | 0.2015 |
| 0.1320 | 0.2514 | 0.6166 | 0.3083 | 0.3316 | 0.3601 |
| | | $T$ = 308.15 K | | | |
| 0.0086 | 0.0000 | 0.9914 | 0.9903 | 0.0000 | 0.0097 |
| 0.0126 | 0.0267 | 0.9607 | 0.9448 | 0.0460 | 0.0092 |
| 0.0156 | 0.0499 | 0.9345 | 0.8832 | 0.1079 | 0.0089 |
| 0.0170 | 0.0637 | 0.9193 | 0.8354 | 0.1439 | 0.0207 |
| 0.0211 | 0.0815 | 0.8974 | 0.7857 | 0.1830 | 0.0313 |
| 0.0237 | 0.0958 | 0.8805 | 0.7202 | 0.2311 | 0.0487 |
| 0.0296 | 0.1173 | 0.8531 | 0.6572 | 0.2740 | 0.0688 |
| 0.0353 | 0.1304 | 0.8343 | 0.6096 | 0.2979 | 0.0925 |
| 0.0390 | 0.1496 | 0.8114 | 0.5524 | 0.3233 | 0.1243 |
| 0.0579 | 0.1844 | 0.7577 | 0.4632 | 0.3492 | 0.1876 |
| 0.1025 | 0.2334 | 0.6641 | 0.3205 | 0.3484 | 0.3311 |
| | | $T$ = 318.15 K | | | |
| 0.0099 | 0.0000 | 0.9901 | 0.9904 | 0.0000 | 0.0096 |
| 0.0142 | 0.0410 | 0.9448 | 0.8937 | 0.0973 | 0.0090 |
| 0.0152 | 0.0543 | 0.9305 | 0.8489 | 0.1425 | 0.0086 |
| 0.0172 | 0.0703 | 0.9125 | 0.7783 | 0.1924 | 0.0293 |
| 0.0189 | 0.0861 | 0.8950 | 0.7304 | 0.2276 | 0.0420 |
| 0.0263 | 0.1175 | 0.8562 | 0.6114 | 0.3045 | 0.0841 |
| 0.0368 | 0.1399 | 0.8233 | 0.5216 | 0.3421 | 0.1363 |
| 0.0431 | 0.1580 | 0.7989 | 0.4710 | 0.3585 | 0.1705 |
| 0.0844 | 0.2177 | 0.6979 | 0.3459 | 0.3651 | 0.2890 |

Compositions in molar fraction.

**Table 3. Experimental Tie-Lines of the System Lim (1) + LiOH (2) + EG (3)**

| EG-Rich Phase | | | Limonene-Rich Phase | | |
|---|---|---|---|---|---|
| $x_1$ | $x_2$ | $x_3$ | $x_1$ | $x_2$ | $x_3$ |
| | | $T$ = 298.15 K | | | |
| 0.0016 | 0.0000 | 0.9984 | 0.9941 | 0.0000 | 0.0059 |
| 0.0018 | 0.0002 | 0.9980 | 0.9538 | 0.0387 | 0.0075 |
| 0.0019 | 0.0034 | 0.9947 | 0.9180 | 0.0722 | 0.0098 |
| 0.0026 | 0.0082 | 0.9892 | 0.8390 | 0.1367 | 0.0243 |
| 0.0019 | 0.0106 | 0.9875 | 0.7863 | 0.1798 | 0.0339 |
| 0.0024 | 0.0107 | 0.9869 | 0.7491 | 0.2045 | 0.0464 |
| 0.0023 | 0.0115 | 0.9862 | 0.7172 | 0.2295 | 0.0533 |
| 0.0026 | 0.0157 | 0.9817 | 0.6258 | 0.2810 | 0.0932 |
| 0.0026 | 0.0189 | 0.9785 | 0.5827 | 0.3080 | 0.1093 |
| 0.0032 | 0.0236 | 0.9732 | 0.4672 | 0.3581 | 0.1747 |
| 0.0033 | 0.0299 | 0.9668 | 0.3354 | 0.3882 | 0.2764 |
| 0.0045 | 0.0424 | 0.9531 | 0.1992 | 0.3739 | 0.4269 |
| | | $T$ = 308.15 K | | | |
| 0.0018 | 0.0000 | 0.9982 | 0.9942 | 0.0000 | 0.0058 |
| 0.0024 | 0.0060 | 0.9916 | 0.8709 | 0.1125 | 0.0166 |
| 0.0021 | 0.0084 | 0.9895 | 0.8154 | 0.1567 | 0.0279 |
| 0.0025 | 0.0111 | 0.9864 | 0.7736 | 0.1893 | 0.0371 |
| 0.0024 | 0.0126 | 0.9850 | 0.7394 | 0.2146 | 0.0460 |
| 0.0017 | 0.0175 | 0.9808 | 0.6239 | 0.2917 | 0.0844 |
| 0.0031 | 0.0219 | 0.9750 | 0.5157 | 0.3434 | 0.1409 |
| 0.0038 | 0.0332 | 0.9630 | 0.3114 | 0.3982 | 0.2904 |
| 0.0051 | 0.0450 | 0.9499 | 0.2013 | 0.3854 | 0.4133 |
| | | $T$ = 318.15 K | | | |
| 0.0018 | 0.0000 | 0.9982 | 0.9937 | 0.0000 | 0.0063 |
| 0.0019 | 0.0002 | 0.9979 | 0.9444 | 0.0479 | 0.0077 |
| 0.0025 | 0.0075 | 0.9900 | 0.8415 | 0.1407 | 0.0178 |
| 0.0020 | 0.0088 | 0.9892 | 0.8141 | 0.1605 | 0.0254 |
| 0.0019 | 0.0126 | 0.9855 | 0.7289 | 0.2258 | 0.0453 |
| 0.0024 | 0.0152 | 0.9824 | 0.6741 | 0.2627 | 0.0632 |
| 0.0031 | 0.0175 | 0.9794 | 0.6281 | 0.2907 | 0.0812 |
| 0.0038 | 0.0217 | 0.9745 | 0.5488 | 0.3315 | 0.1197 |
| 0.0031 | 0.0312 | 0.9657 | 0.3553 | 0.4041 | 0.2406 |
| 0.0041 | 0.0429 | 0.9530 | 0.2217 | 0.4006 | 0.3777 |

Compositions in molar fraction.

obtained parameters are used in the second objective function, $F_b$, to fit the experimental concentrations:

$$F_a = \sum_k \sum_i \sum_j [(a^I_{ijk} - a^{II}_{ijk})/(a^I_{ijk} + a^{II}_{ijk})]^2 + Q \sum_n P_n^2 \quad (1)$$

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

where $x$ is the experimental mole fraction, $\hat{}$ stands for the calculated properties, $a$ is the activity, $i$ are the components of the mixture, $j$ are the phases, and $k$ are the tie-lines. Both functions include a penalization term (the second term) to reduce the risks of multiple solutions associated with parameters of high value, in which $Q$ is a constant and $P_n$ are the adjustable parameters. $F_b$ also includes a term to ensure that the parameters give a solute distribution ratio at infinite dilution that approximates to a value previously defined by the user, $\beta_\infty$, and $\hat{\gamma}^I_{S,\infty}$ and $\hat{\gamma}^{II}_{S,\infty}$ represent the solute activity coefficients calculated at infinite dilution in both phases.

Quality of the correlation was measured by the residual function $F$ and by the mean error of the solute distribution ratio, $\Delta\beta$:

$$F = 100 \times \left[\sum_k \min \sum_i \sum_j \frac{(x_{ijk} - \hat{x}_{ijk})^2}{6M}\right]^{0.5} \quad (3)$$

**Table 4. Experimental Tie-Lines of the System Lim (1) + LiOH (2) + [emim][OMs] (3)**

| [emim][OMs]-Rich Phase | | | Limonene-Rich Phase | | |
|---|---|---|---|---|---|
| $x_1$ | $x_2$ | $x_3$ | $x_1$ | $x_2$ | $x_3$ |
| | | $T$ = 298.15 K | | | |
| 0.0022 | 0.0188 | 0.9790 | 0.9543 | 0.0457 | 0.0000 |
| 0.0074 | 0.0652 | 0.9275 | 0.8983 | 0.1004 | 0.0013 |
| 0.0078 | 0.0793 | 0.9128 | 0.8724 | 0.1255 | 0.0021 |
| 0.0119 | 0.0996 | 0.8886 | 0.8570 | 0.1390 | 0.0040 |
| 0.0409 | 0.1786 | 0.7805 | 0.8155 | 0.1716 | 0.0129 |
| 0.0193 | 0.1278 | 0.8529 | 0.8402 | 0.1532 | 0.0065 |
| 0.0484 | 0.1885 | 0.7631 | 0.8157 | 0.1727 | 0.0115 |
| 0.1891 | 0.2884 | 0.5225 | 0.7916 | 0.1873 | 0.0211 |
| 0.3880 | 0.3183 | 0.2936 | 0.7344 | 0.2173 | 0.0482 |

Compositions in molar fraction.

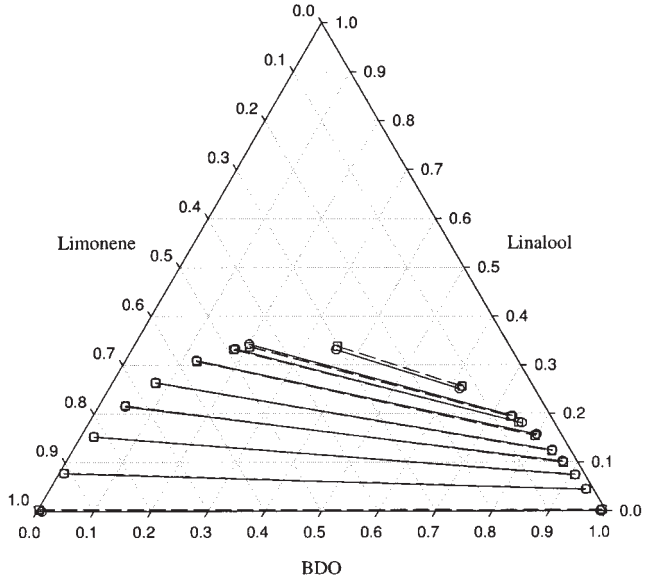


**Figure 2. Experimental tie lines (○———○) and NRTL ($\alpha$ = 0.2) correlation (□— — —□) at 298.15 K for Lim + LiOH + BDO.**

$$\Delta\beta = 100 \times \left[ \sum_k \frac{((\beta_k - \hat{\beta}_k)/\beta_k)^2}{M} \right]^{0.5} \quad (4)$$

where $M$ is the total number of tie-lines.

Correlation can be done in two ways: without defining an a priori value of $\beta_\infty$, and specifying an optimal value of this parameter, previously found by trial and error considering the minimization of $\Delta\beta$ as the optimality criterion. Usually when $\beta_\infty$ is defined, the residual $\Delta\beta$ decreases extensively, and the residual $F$ in the worse cases slightly increases.[30] This behavior

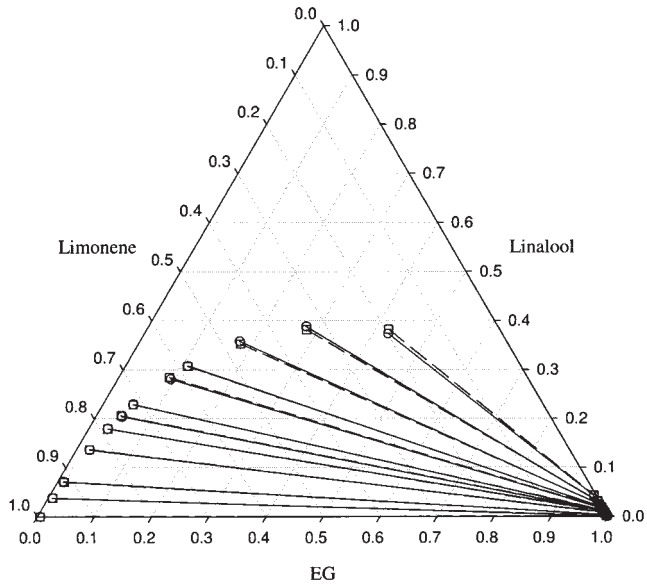


**Figure 3. Experimental tie lines (○———○) and NRTL ($\alpha$ = 0.1) correlation (□— — —□) at 298.15 K for Lim + LiOH + EG.**

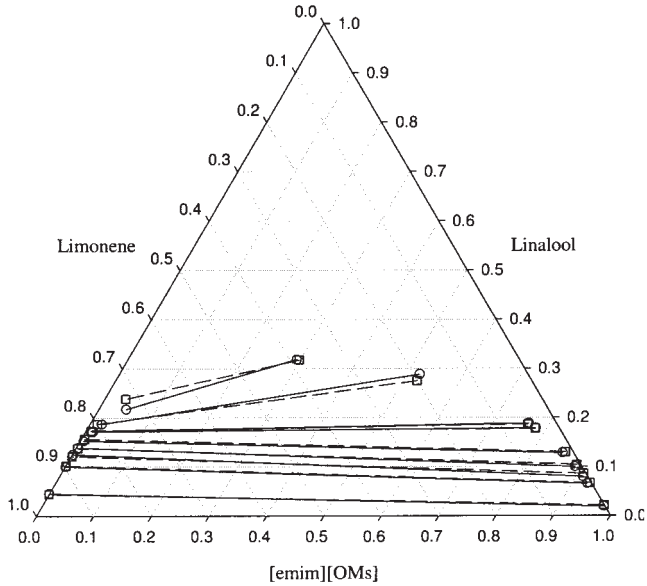


**Figure 4. Experimental tie lines (○———○) and NRTL ($\alpha$ = 0.1) correlation (□— — —□) at 298.15 K for Lim + LiOH + [emim][OMs].**

was found in the systems with organic solvents. Nevertheless, in the system with the RTIL, the best results correspond to correlation without $\beta_\infty$ optimization. Tables 5, 6, and 7 show the correlation residual and parameters for each system. A comparison of the experimental data and the best NRTL correlation can be seen in Figures 2, 3, and 4.

### *Solvent evaluation*

The ability of both the organic solvents and the RTIL to extract the linalool from the essential oil mixture was evaluated from the experimental data at 298.15 K using the solute distribution ratio, $\beta_{LiOH}$, and the selectivity, $S$:

$$\beta_{LiOH} = \frac{(w_{LiOH})^{Solvent}}{(w_{LiOH})^{LiM}} \quad (5)$$

$$S = \frac{(w_{LiOH})^{Solvent} \cdot (w_{LiM})^{LiM}}{(w_{LiOH})^{LiM} \cdot (w_{LiM})^{Solvent}} = \frac{\beta_{LiOH}}{\beta_{LiM}} \quad (6)$$

**Table 5. NRTL ($\alpha$ = 0.2) Correlation (Using the Optimal Value of $\beta_\infty$) for Lim (1) + LiOH (2) + BDO (3): Residuals and Parameters**

| $i$ | $j$ | $\Delta g_{ij}$ | $\Delta g_{ji}$ | |
|---|---|---|---|---|
| | | | | $T$ = 298.15 K |
| 1 | 2 | 10628 | −6066.1 | $\beta_\infty$ = 0.81 |
| 1 | 3 | 10571 | 8660.7 | $\Delta\beta$ = 1.66% |
| 2 | 3 | 3549.0 | −1284.8 | $F$ = 0.2905% mol |
| | | | | $T$ = 308.15 K |
| 1 | 2 | 10950 | −6249.5 | $\beta_\infty$ = 0.72 |
| 1 | 3 | 11428 | 8639.9 | $\Delta\beta$ = 2.08% |
| 2 | 3 | 1970.9 | 103.33 | $F$ = 0.2423% mol |
| | | | | $T$ = 318.15 K |
| 1 | 2 | 11950 | −6631.6 | $\beta_\infty$ = 0.68 |
| 1 | 3 | 12099 | 8790.3 | $\Delta\beta$ = 2.52% |
| 2 | 3 | 2405.1 | 202.47 | $F$ = 0.3271% mol |

Table 6. NRTL ($\alpha = 0.1$) Correlation (Using the Optimal Value of $\beta_\infty$) for Lim (1) + LiOH (2) + EG (3): Residuals and Parameters

| $i$ | $j$ | $\Delta g_{ij}$ | $\Delta g_{ji}$ | |
|---|---|---|---|---|
| | | | | $T = 298.15$ K |
| 1 | 2 | −3022.4 | 294.24 | $\beta_\infty = 0.04$ |
| 1 | 3 | 6531.4 | 9367.9 | $\Delta\beta = 25.83\%$ |
| 2 | 3 | −8946.6 | 18282 | $F = 0.2162\%$ mol |
| | | | | $T = 308.15$ K |
| 1 | 2 | −3819.4 | 1464.9 | $\beta_\infty = 0.04$ |
| 1 | 3 | 7029.9 | 9269.8 | $\Delta\beta = 3.52\%$ |
| 2 | 3 | −8754.6 | 18052 | $F = 0.1930\%$ mol |
| | | | | $T = 318.15$ K |
| 1 | 2 | −3465.9 | 713.02 | $\beta_\infty = 0.04$ |
| 1 | 3 | 7488.6 | 9304.7 | $\Delta\beta = 28.31\%$ |
| 2 | 3 | −8851.0 | 18389 | $F = 0.1860\%$ mol |

where $w$ represents the mass fraction of each component. The results obtained are shown in Figures 5 and 6. The figures also show results for other solvents previously studied[16-18]: diethylene glycol (DEG), 1,2-propanediol (12PDO), 1,3-propanediol (13PDO), and 2-aminoethanol (AE).

A good solvent for liquid extraction should have $\beta > 1$ and the highest value for $S$. Direct inspection of Figure 5 shows that only the RTIL [emim][OMs] and 12PDO have a favorable solute distribution ratio, $\beta_{LiOH}$. But not in the entire immiscible region: only for high and low linalool concentrations, respectively. This change of $\beta_{LiOH}$ in the [emim][OMs] system is due to the change in the tie-lines' slope, solutropy. Figure 6 shows also that the [emim][OMs] provides the best values for selectivity in the whole immiscible region. Nevertheless, difference with the organic solvents is very small as they also have a favorable value of $S$.

### *Liquid extraction simulation*

With the aim to analyze the possibility of carrying out citrus essential oil terpenless by liquid-liquid extraction, simulation of the process was done using the HYSYS® (v3.2) software from Aspen Technology, Inc. (Cambridge, MA). Liquid extractor was the operation unit selected, and the program solved the MESH equations (Material balances, Equilibrium relationships, Summation molar fractions, Heat balances). In order to obtain the equilibrium data, parameters of the best NRTL correlation at 298.15 K were used. Operation was isothermal at 298.15 K and 101.32 kPa. Feed simulated had a 35 wt% linalool and a 100 kg·h$^{-1}$ mass flow. Solvent mass flow was varied in order to get a solvent-to-feed ratio, *S/F*, ranging from 0.25 to 1.5. Then the mass flow for each component was computed for different equilibrium stages, $N$, ranging from 1 up to 15. Finally, the total linalool extracted (*%Ext*) and the linalool composition in the extracted product (*%EP*, extract without solvent) were calculated as:

Table 7. NRTL ($\alpha = 0.1$) Correlation (Not Fixing Any Value of $\beta_\infty$) for Lim (1) + LiOH (2) + [emim][OMs] (3): Residuals and Parameters

| $i$ | $j$ | $\Delta g_{ij}$ | $\Delta g_{ji}$ | |
|---|---|---|---|---|
| 1 | 2 | 23206 | −15955 | $T = 298.15$ K |
| 1 | 3 | 14091 | 20165 | $\Delta\beta = 8.19\%$ |
| 2 | 3 | −3166.3 | −6201.8 | $F = 0.5224\%$ mol |

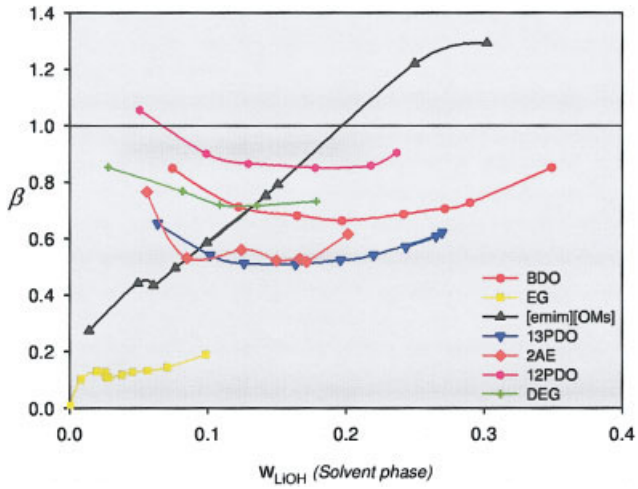


**Figure 5. Linalool solute distribution ratio, $\beta_{LiOH}$, between different solvents and limonene at 298.15 K.**

Lines shown to facilitate identification, without physical meaning. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

$$\%Ext = \frac{(m_{LiOH})^{Extract}}{(m_{LiOH})^{Feed}} \times 100 \tag{7}$$

$$\%EP = \frac{(m_{LiOH})^{Extract}}{(m_{LiOH} + m_{Lim})^{Extract}} \times 100 \tag{8}$$

where $m$ stands for mass flows, and there are subscripts for components (*LiOH* for linalool and *Lim* for limonene) and superscripts for the different currents in the extraction process (*Extract* and *Feed*). Figure 7 shows the results for [emim][OMs], BDO, and 12PDO. The *%Ext* and *%EP* surfaces

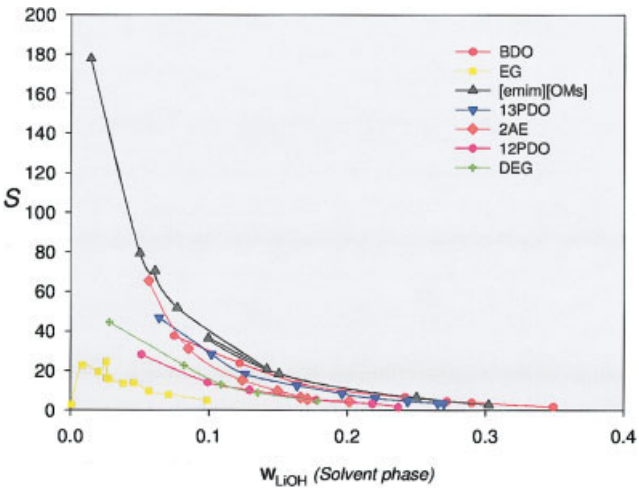


**Figure 6. Selectivity, *S*, for different solvents to extract linalool from its mixtures with limonene at 298.15 K.**

Lines shown to facilitate identification, without physical meaning. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

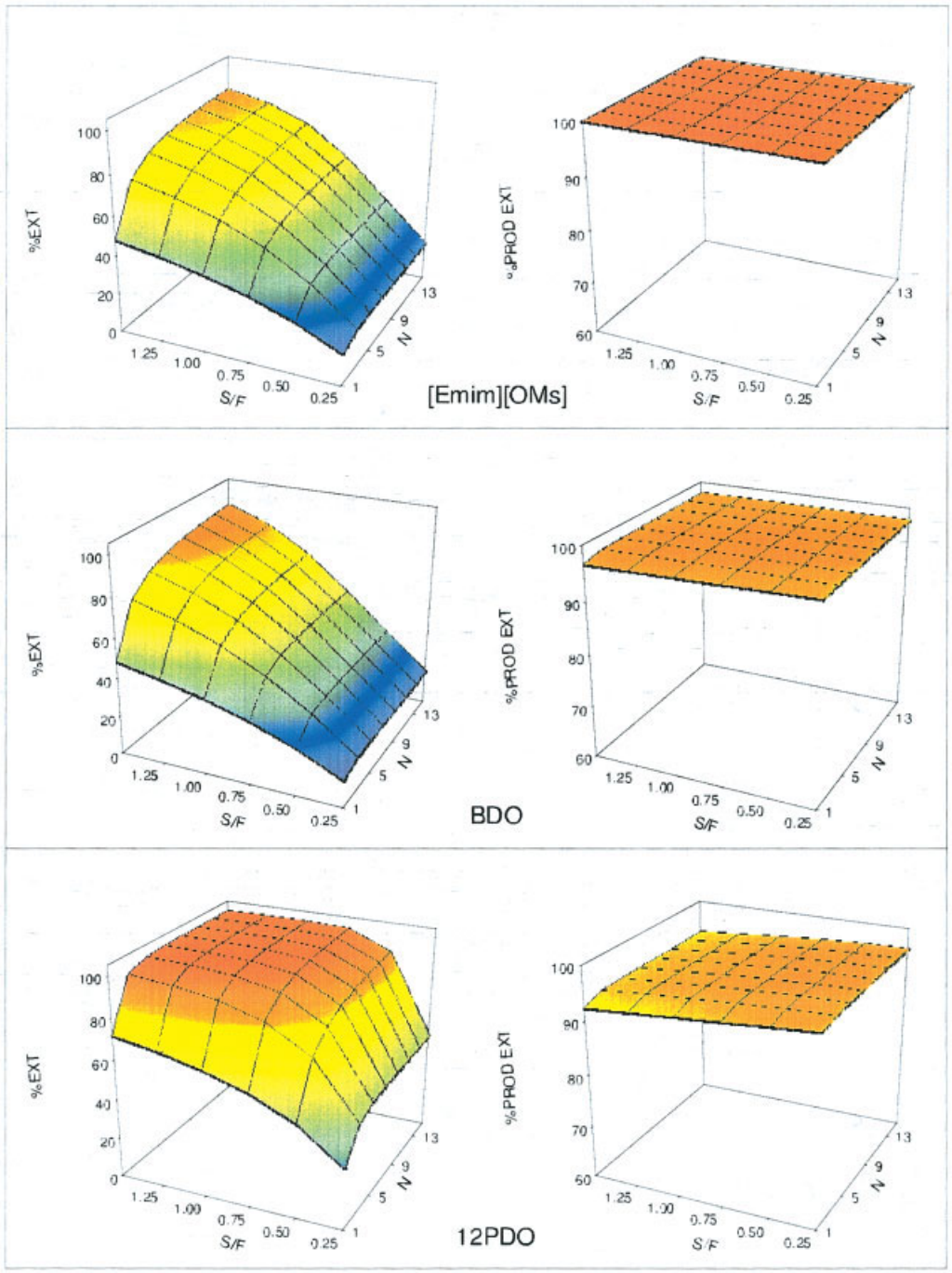


**Figure 7. Linalool extracted (%*Ext*, left) and linalool composition in the extracted product (%*EP*, right) as a function of the solvent-to-feed ratio, *S/F*, and number of equilibrium stages, *N*.**

Solvents used, from top to bottom: [emim][OMs], BDO, 12PDO. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

are plotted against the number of equilibrium stages, *N*, and the solvent-to-feed ratio, *S/F*.

## Conclusions

Search for an effective method for essential oils terpenless is necessary. As delicate oils can be damaged by distillation, liquid extraction seems to be a good alternative. In this work, the validity of different solvents to carry out this separation has been analyzed. Analysis has been focused from a thermodynamic point of view.

Selected solvents were 2-butene-1,4-diol (BDO) and ethylene glycol (EG), chosen according to the acquired experience in our previous research on this subject. It has been necessary to determine the liquid-liquid equilibria for Lim + LiOH + (BDO or EG) systems, which was done at 298.15, 308.15, and 318.15 K. It has been found that temperature shows nearly no

influence on the tie-lines' size or slope in the temperature range studied.

Due to the big advantages of ionic liquids as green solvents on extraction processes, the last solvent used in this study was 1-ethyl-3-methylimidazolium methanesulfonate ([emim]-[OMs]). Data for the Lim + LiOH + [emim][OMs] system were obtained at 298.15 K.

Correlation of LLE experimental data is commonly desirable as it allows interpolation of tie-lines in the immiscible region of the system. Thus, equilibrium data can be easily managed for design purposes. For this reason, experimental data have been correlated using the NRTL equation and results were satisfactory. The nonrandomness parameter, $\alpha$, was fixed to 0.1, 0.2, and 0.3. The best results were obtained with $\alpha = 0.2$ for the BDO system and $\alpha = 0.1$ for both the EG and [emim][OMs] systems. Optimization of $\beta_\infty$ leads to different results. The EG system has the expected behavior and the residual $\Delta\beta$ is importantly reduced at the cost of a slight increase in the residual $F$. The BDO system reduced both residuals, $\Delta\beta$ and $F$. The [emim][OMs] system increased both residuals, so the correlation with non-optimized $\beta_\infty$ was selected.

Solvent selection, from compounds presented here and some others obtained in previous works, by means of the solute distribution ratio, $\beta_{LiOH}$, and the selectivity, $S$, is difficult. [emim][OMs] shows favorable distribution ratios ($\beta_{LiOH} > 1$) in the rich-linalool region, but its values are non-favorable in the rest of the heterogeneous area. 12PDO has the highest values on average, but it still has non-favorable distribution ratios ($\beta_{LiOH} < 1$) except in the low-linalool region. Despite the poor distribution ratios for these solvents, their selectivity, $S$, is favorable in all cases. This is due to the low mutual solubilities of limonene and the solvents, which enhances the $S$ value. Among the solvents, the ionic liquid and the BDO show the best values for this parameter. But differences between solvents are small. Despite its good values for $\beta_{LiOH}$, 12PDO does not present such a good selectivity.

Solvents selected for the extraction simulation were 12PDO, BDO, and [emim][OMs], due to their high value in the parameters studied. The extraction simulation shows that 12PDO presents higher *%Ext* than the ionic liquid [emim][OMs] and BDO. This is due to the higher linalool distribution ratio among this solvent. Maximum linalool recovery using [emim][OMs] or BDO is around 90%. Nevertheless, purity of the extracted product (after solvent separation) would be much higher using the ionic liquid: *%EP* is about 100%. BDO also provides a *%EP* around 97% at any conditions. But *%EP* for 12PDO has lower values, ranging from 92 to 96%. This is due to its lower selectivity, as the solvent carries more limonene than the others. Then solvent selection must choose between the highest extraction capacity of 12PDO, with a lower purity (more limonene impurities), or the highest purity attained by [emim][OMs] with a lower linalool recovery.

It has to be stated that these are just preliminary results based on thermodynamic behavior. Solvent selection must take into account other parameters, such as economics, safety, toxicity, and so on. An interesting alternative is now opened with RTILs; their negligible vapor pressure facilitates solvent recovery after the extraction process. Moreover, in addition to their interesting environmental and safety properties, many different cations and anions can be used to synthesize the RTIL, so the RTIL properties can be "designed" by use of different selected combinations of anions and cations. Thus, extraction and solvent properties could be further optimized.

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