JOURNAL OF CHEMICAL & ENGINEERING DATA

ARTICLE

pubs.acs.org/jced

Deterpenation of Bergamot Essential Oil Using Liquid−Liquid Extraction: Equilibrium Data of Model Systems at 298.2 K

Cristina Chiyoda,[†] Maria C. Capellini,[†] Ivana M. Geremias,[†] Fernanda H. Carvalho,[†] Keila K. Aracava,[†] Rachel S. Bueno,[‡] Cintia B. Gonçalves,[†] and Christianne E. C. Rodrigues*[,†]

Separation Engineering Laboratory − (LES), [†]Department of Food Engineering (ZEA-FZEA), and [‡]Department of Basic Sciences (ZAB − FZEA), University of São Paulo (USP), P.O. Box 23, Zip Code 13635-900, Pirassununga, SP, Brazil

ABSTRACT: The deterpenation of bergamot essential oil can be performed by liquid−liquid extraction using hydrous ethanol as the solvent. A ternary mixture composed of 1-methyl-4-prop-1-en-2-yl-cyclohexene (limonene), 3,7-dimethylocta-1,6-dien-3-yl-acetate (linalyl acetate), and 3,7-dimethylocta-1,6-dien-3-ol (linalool), three major compounds commonly found in bergamot oil, was used to simulate this essential oil. Liquid−liquid equilibrium data were experimentally determined for systems containing essential oil compounds, ethanol, and water at 298.2 K and are reported in this paper. The experimental data were correlated using the NRTL and UNIQUAC models, and the mean deviations between calculated and experimental data were lower than 0.0062 in all systems, indicating the good descriptive quality of the molecular models. To verify the effect of the water mass fraction in the solvent and the linalool mass fraction in the terpene phase on the distribution coefficients of the essential oil compounds, nonlinear regression analyses were performed, obtaining mathematical models with correlation coefficient values higher than 0.99. The results show that as the water content in the solvent phase increased, the *k* value decreased, regardless of the type of compound studied. Conversely, as the linalool content increased, the distribution coefficients of hydrocarbon terpene and ester also increased. However, the linalool distribution coefficient values were negatively affected when the terpene alcohol content increased in the terpene phase.

INTRODUCTION

Recently, essential oils have become important in the global economy not only for their medicinal properties but also due to their wide use in the chemical and food industries.[1] According to the United Nations Commodity Trade Statistics Database (UN Comtrade Web site),[2] the total world exports value of essential oils in 2009 was approximately US$ 1,989 billion, and the five largest exporters were the United States (23.00%), France (11.20%), the United Kingdom (10.50%), Germany (9.10%), and Switzerland (6.20%). Regarding imports, the total amount was US$ 2,138 billion and the largest importers were the United States (19.00%), India (13.00%), France (12.00%), Argentina (6.60%), Brazil (5.90%), and the United Kingdom (6.60%).[2]

Essential oils are complex mixtures composed of more than 100 compounds, including highly volatile components that represent more than 90% of the oil; these compounds include terpenes, sesquiterpenes, and oxygenated compounds, which are mainly responsible for the aroma in the essential oil. The mixtures also contain nonvolatile compounds, such as pigments and waxes.[3]

Bergamot (*Citrus bergamia* Risso) is a typical fruit in South Italy, and its essential oil is obtained by pressing the fruit peel.[4] Franceschi et al.[5] reported the composition of bergamot essential oil, of which the main components are limonene (38.2%), linalyl acetate (34.7%), linalool (15.3%), γ-terpinene (4.1%), and β-pinene (3.1%).

Although this oil naturally contains a large number of oxygenated compounds in its composition compared to other essential oils, terpenic hydrocarbon removal is still necessary. This removal process, known as deterpenation, increases the oxidative stability of the oil because the terpenic hydrocarbons decompose when heated or exposed to air, resulting in products with lower sensorial quality.[6]

Several methods for essential oils deterpenation, such as supercritical fluid extraction,[7,8] membrane processing,[9,10] supercritical adsorption/desorption,[11,12] vacuum and steam-distillations,[13,14] enzymatic conversion,[15,16] selective inclusion,[6] and solvent (or liquid−liquid) extraction[17−19] have been proposed.

The liquid−liquid extraction (LLE) method is based on the difference in solubility between terpenes and oxygenated compounds in a given solvent. Compared to other methods, this process presents advantages such as lower water and energy consumption and lower cost because it is performed under mild temperature and pressure conditions.[20]

Ionic liquids,[17,21] glycols,[22−24] water,[25,26] aminoethanol,[27] acetonitrile, nitromethane and dimethylformamide,[28] and short chain alcohols such as methanol,[19,29,30] ethanol,[1,18,26,31−34] propanol, and butanol[35] have been reported as potential solvents in the liquid extraction processes.

Among the mentioned solvents, ethanol is highlighted because alcoholic extracts have vast industrial applications. Alcoholic extracts are highly soluble in water solutions and may be easily diluted in beverages and perfumes. The components of essential oils have their aromatic and stability characteristics enhanced as alcoholic solutions, as oxidizing reactions are reduced with ethanol.[31]

In this work, liquid−liquid equilibrium data for systems containing limonene, linalyl acetate, linalool, ethanol, and water are reported. Experimental data were collected at (298.2 ± 0.1) K, and the alcoholic solvents contained high levels of water mass fraction, which reached up to 0.42. The experimental data

Received: December 17, 2010
Accepted: February 24, 2011
Published: March 14, 2011

Table 1. Molar Masses, CAS Registry Numbers, Experimental Purities,[a] and Structural Parameters, r_i and q_i

compound	M[b]/g·mol^{-1}	CAS registry no.	purity[c]	r_i[d]	q_i[e]
1-methyl-4-prop-1-en-2-yl-cyclohexene (1)	136.23	5989-27-5	0.9995	0.0461	0.0382
3,7-dimethylocta-1,6-dien-3-yl-acetate (2)	196.29	115-95-7	0.9888	0.0428	0.0367
3,7-dimethylocta-1,6-dien-3-ol (3)	154.24	78-70-6	0.9977	0.0487	0.0433
Ethanol (4)	46.07	64-17-5	0.9981	0.0559	0.0562
Water (5)	18.02	7732-18-5		0.0511	0.0777

[a] Supplied by the author. [b] Molar mass. [c] Experimentally determined by gas chromatography, given as mass fractions. [d] Volume structural parameter, calculated according to eq 6. [e] Area structural parameter, calculated according to eq 6.

presented in this work were correlated using the NRTL[36] and UNIQUAC[37] thermodynamic equations with an estimation of binary interaction parameters.

In addition, complete second-order models were adjusted to the experimental data in an effort to better understand the effect of process variables (water mass fraction in the solvent, and the linalool mass fraction in the terpene phase) on the distribution coefficients of the essential oil compounds.

EXPERIMENTAL SECTION

Materials. In this work, aqueous solvents with water mass fractions of 0.2849, 0.3085, 0.3357, and 0.4215 were used; the solvents were prepared by diluting absolute ethanol (Merck), with a mass fraction purity higher than 0.998, into deionized water (Millipore, Milli-Q, Bedford, MA, U.S.A.).

All essential oil reagents used in this study, 1-methyl-4-prop-1-en-2-yl-cyclohexene (limonene, Sigma-Aldrich), 3,7-dimethylocta-1,6-dien-3-ol (linalool, Sigma-Aldrich), and 3,7-dimethylocta-1,6-dien-3-yl-acetate (linalyl acetate, Sigma-Aldrich), were analyzed by gas chromatography GC-FID (Shimadzu, model GC 2010 AF) with an automatic injector (Shimadzu, model AOC 20i) to determine the experimental purities and retention times of the compounds according to the following experimental conditions: DB-FFAP capillary (nitroterephthalic acid-modified polyethylene glycol) column (Agilent) 0.25 μm, 30 m × 0.25 mm i.d.; helium as the carrier gas at the rate of 1.13 mL·min^{-1}; injection temperature of 553.2 K; column temperature of (373.2 to 443.2) K (rate of 4 K·min^{-1}); detection temperature of 553.2 K; injection volume of 1.0 μL.

Details concerning the CAS registry number and experimental purity for each essential oil compound can be found in Table 1.

The following notations were given to the components utilized in the experiments: limonene (1), linalyl acetate (2), linalool (3), ethanol (4), and water (5).

Apparatus and Procedures. The study of phase equilibrium was carried out according to the methodology described by Rodrigues et al.[38] The stock solutions were prepared containing limonene and linalyl acetate at a mass ratio of 1.10:1. This mass ratio between the terpene and ester compounds was adopted on the basis of the experimental composition of bergamot oil published by Franceschi et al.[5]

The model systems were prepared by diluting known quantities of linalool into the stock solution. These model systems were mixed with the ethanolic solvents at a 1:1 mass ratio at (298.2 ± 0.1) K to determine liquid–liquid equilibrium data, which were used to adjust NRTL and UNIQUAC parameters.

The components were weighed on an analytical balance (Adam, model PW 254, Milton Keynes, U.K.), with a readability and accuracy of 0.0001 g, directly into 15 mL polypropylene centrifuge tubes (Corning Inc.). The tubes were vigorously stirred at 2800 rpm for at least 10 min at room temperature (quite close to 298 K), centrifuged for 20 min at 5000 g at (298.2 ± 1.5) K in a centrifuge equipped with a temperature controller (Thermo Electron Corp., model CR3i) and then placed in a thermostatic bath at (298.2 ± 0.1) K for 20 h (Marconi, model MA-184).

After this treatment, the two phases were clearly separated with a well-defined interface.

Samples from both top (terpene rich phase) and bottom (solvent rich phase) phases were collected separately using syringes, and the compositions of both phases were measured. The contents of the essential oil compounds (limonene, linalyl acetate, and linalool) and ethanol were determined by gas chromatography GC-FID (Shimadzu, model GC 2010 AF) with an automatic injector (Shimadzu, model AOC 20i) using the same experimental conditions previously described. The components were identified by comparison against the retention times of pure compounds, and quantification was performed using the external standard method. Water content was determined by Karl Fischer titration (Metrohm, 787 KF Titrino, Switzerland) using Karl Fischer reagent purchased from Merck.

In this work, all measurements were performed at least in triplicate. Type A standard uncertainties[39] of the equilibrium data, in mass fraction, ranged from (0.0001 to 0.0241) for limonene, (0.0001 to 0.0199) for linalyl acetate, (0.0001 to 0.0076) for linalool, (0.0001 to 0.0132) for ethanol and, (0.0001 to 0.0175) for water. In the aforementioned data set, the lowest values were obtained from the lowest mass fractions.

To evaluate the validity of results, the procedure developed by Marcilla et al.[40] was employed. According to this approach, i independent component balances can be written as follows, with i representing each component of the system:

$$M^{\mathrm{OC}} \cdot w_i^{\mathrm{OC}} = M^{\mathrm{TP}} \cdot w_i^{\mathrm{TP}} + M^{\mathrm{SP}} \cdot w_i^{\mathrm{SP}} \qquad (1)$$

where M^{OC} represents the amount of the initial mixture; M^{TP} and M^{SP} represent the amounts of the terpene phase (top phase) and solvent phase (bottom phase), respectively; w_i^{OC} represents the mass fraction of component i in the initial mixture; and w_i^{TP} and w_i^{SP} represent the mass fractions of component i in the terpene and solvent phases, respectively.

With these i equations, it is possible to calculate the values of M^{TP} and M^{SP} from the experimental values w_i^{TP} and w_i^{SP} by a least-squares fitting. If $\mathbf{M}$ represents the matrix composed of w_i^{OC} values, $\mathbf{B}$ represents the transformation matrix (composed of w_i^{TP} and w_i^{SP} values) and $\mathbf{P}$ represents the matrix composed of the amounts of each phase (M^{TP} and M^{SP}), then the previous system can be written as

$$\mathbf{M} = \mathbf{B} \cdot \mathbf{P} \qquad (2)$$

Mathematic calculations lead to the following expression (eq 3),

$$\mathbf{P} = (\mathbf{B}^{\mathrm{T}}\mathbf{B})^{-1}\mathbf{B}^{\mathrm{T}}\mathbf{M} \qquad (3)$$

where $\mathbf{B}^{\mathrm{T}}$ represents the transpose matrix of $\mathbf{B}$ and $(\mathbf{B}^{\mathrm{T}}\mathbf{B})^{-1}$ represents the inverse matrix of $(\mathbf{B}^{\mathrm{T}}\mathbf{B})$. Therefore, the values of M^{TP} and M^{SP} (matrix $\mathbf{P}$), which minimize the errors of the previous system, have been calculated.

Deviations (δ) between the sum $(M^{\mathrm{TP}} + M^{\mathrm{SP}})$ and M^{OC} (the amount of the initial mixture) can be calculated according to eq 4.

$$\delta = (|(M^{\mathrm{TP}} + M^{\mathrm{SP}}) - M^{\mathrm{OC}}|/M^{\mathrm{OC}}) \times 100 \qquad (4)$$

The relative deviation of the mass balance for each compound i (δ_i) can be calculated according to eq 5 in each equilibrium experiment.

$$\delta_i = (|(M^{\mathrm{TP}}w_i^{\mathrm{TP}} + M^{\mathrm{SP}}w_i^{\mathrm{SP}}) - M^{\mathrm{OC}}w_i^{\mathrm{OC}}|/M^{\mathrm{OC}}w_i^{\mathrm{OC}}) \times 100 \qquad (5)$$

The relative deviation (δ) of the results was lower than 0.7%, indicating a high precision and repeatability of the equilibrium data.[20,41]

Thermodynamic Modeling Procedure. The determined experimental data were used to adjust the NRTL and UNIQUAC binary interaction parameters. Mole fractions have traditionally been used in these models, but mass fractions provide a more convenient composition unit due to the difference in the molar masses of the components such as terpenes, ethanol, and water (see Table 1). Recently, several studies have reported using this approach with the NRTL and UNIQUAC models.[38,41−46]

Rodrigues et al.[47] show the activity coefficient equations, expressed in mass fractions, according to the NRTL and UNIQUAC models.

The r_i and q_i values, the volume and area parameters, properly converted to be used in the UNIQUAC model expressed in mass fractions, were calculated via eq 6, where $\nu_k^{(i)}$ represents the number of groups k in the molecule of component i, M_i represents the molar mass of compound i, G represents the total number of groups, and R_k and Q_k represent the van der Waals parameters obtained from Magnussen et al.[48]

$$r_i = \frac{1}{M_i}\sum_k^G \nu_k^{(i)} R_k \qquad q_i = \frac{1}{M_i}\sum_k^G \nu_k^{(i)} Q_k \qquad (6)$$

Therefore, in the present study, there are three adjustable parameters for each pair of components for the NRTL model and two adjustable parameters for the UNIQUAC model.

The estimation of the interaction parameters was based on the minimization of the objective function of composition (eq 7) according to the algorithm developed in FORTRAN language by Stragevitch and d'Avila.[49]

$$\mathrm{OF}(w) = \sum_{m=1}^{D}\sum_{n=1}^{N}\sum_{i=1}^{K-1}\left[\left(\frac{w_{i,n,m}^{\mathrm{TP,exptl}} - w_{i,n,m}^{\mathrm{TP,calcd}}}{\sigma_{w_{i,n,m}^{\mathrm{TP}}}}\right)^2 + \left(\frac{w_{i,n,m}^{\mathrm{SP,exptl}} - w_{i,n,m}^{\mathrm{SP,calcd}}}{\sigma_{w_{i,n,m}^{\mathrm{SP}}}}\right)^2\right] \qquad (7)$$

where D represents the total number of data groups, N represents the total number of tie lines, and K represents the total number of components in the group of data m. w represents the mass fraction; the subscripts i, n, and m represent the component, tie line, and group number, respectively, and the superscripts TP and SP represent terpene and solvent phases, respectively. exptl and calcd refer to experimental and calculated compositions. $\sigma_{w_{i,n,m}^{\mathrm{TP}}}$ and $\sigma_{w_{i,n,m}^{\mathrm{SP}}}$ represent the standard deviations observed in the compositions of the two liquid phases.

The deviations between experimental and calculated compositions in both phases were calculated according to eq 8.

$$\Delta w = \sqrt{\frac{\sum_{n=1}^{N}\sum_{i=1}^{K}[(w_{i,n}^{\mathrm{TP,exptl}} - w_{i,n}^{\mathrm{TP,calcd}})^2 + (w_{i,n}^{\mathrm{SP,exptl}} - w_{i,n}^{\mathrm{SP,calcd}})^2]}{2NK}} \qquad (8)$$

Statistical Analysis. Statistical analysis was used to investigate the effect of certain process variables (water mass fraction in the solvent, w_{5S}, and the linalool mass fraction in the terpene phase, w_3^{TP}) on the distribution coefficients of the essential oil compounds (k_i, calculated according to eq 9) during an equilibrium stage of the liquid−liquid extraction deterpenation process.

$$k_i = \frac{w_i^{\mathrm{SP}}}{w_i^{\mathrm{TP}}} \qquad (9)$$

where w represents the mass fraction, and the superscripts SP and TP represent the solvent and terpene phases, respectively.

Complete second-order models, which are represented by eq 10, were adjusted to the experimental data using the nonlinear (NLIN) procedure of Statistical Analysis Software (SAS, version 9.2), considering the coefficient of correlation (R), analysis of variance, F test, and physical interpretation of the parameters. The following three treatments were considered: water mass fraction in the solvent (linear and quadratic), linalool mass fraction in the terpene phase (linear and quadratic), and the interaction between both treatments. The parameters of nonlinear models were estimated by the least-squares fitting method.

$$k_i = \beta_0 + \beta_1 w_{5S} + \beta_2 (w_{5S})^2 + \beta_3 w_3^{\mathrm{TP}} + \beta_4 (w_3^{\mathrm{TP}})^2 + \beta_5 w_3^{\mathrm{TP}} w_{5S} \qquad (10)$$

where k_i is the distribution coefficient, β_n (n = 0−5) are the parameters estimated, w_{5S} is the water mass fraction in the solvent linear effect, $(w_{5S})^2$ is the water mass fraction in the solvent quadratic effect, w_3^{TP} is the linalool mass fraction in the terpene phase linear effect, $(w_3^{\mathrm{TP}})^2$ is the linalool mass fraction in the terpene phase quadratic effect, and $w_3^{\mathrm{TP}} w_{5S}$ is the interaction between both variables.

To evaluate the predictive capacity of the statistical models, the average relative deviations (ARD) were calculated according to eq 11,

$$\mathrm{ARD} = \left[\sum_{i=1}^{n}\left(\frac{|k_i^{\mathrm{exptl}} - k_i^{\mathrm{est}}|}{k_i^{\mathrm{exptl}}}\right)\right] \times \frac{1}{n} \qquad (11)$$

where k_i represents the distribution coefficient, n represents the number of experimental data, and the superscripts exptl and est are related to the experimental values and those estimated using the statistical models, respectively.

RESULTS

As previously stated, a ternary mixture composed of limonene, linalyl acetate, and linalool was used to simulate bergamot essential oil. Thus, liquid−liquid equilibrium experimental data for systems containing these compounds and aqueous solvents

Table 2. Liquid−Liquid Equilibrium Data for Systems of Limonene (1) + Linalyl Acetate (2) + Linalool (3) + Ethanol (4) + Water (5), at (298.2 ± 0.1) K

	overall composition					terpene rich phase					solvent rich phase				
w_{5S}[a]	w_1	w_2	w_3	w_4	w_5	w_1	w_2	w_3	w_4	w_5	w_1	w_2	w_3	w_4	w_5
0.2849	0.2620	0.2379	0.0000	0.3576	0.1425	0.4771	0.3780	0.0000	0.1278	0.0171	0.0411	0.0795	0.0000	0.6072	0.2722
	0.2484	0.2256	0.0257	0.3577	0.1426	0.4332	0.3496	0.0332	0.1597	0.0243	0.0440	0.0800	0.0176	0.5814	0.2770
	0.2357	0.2141	0.0501	0.3576	0.1425	0.3861	0.3163	0.0649	0.1982	0.0345	0.0445	0.0753	0.0326	0.5724	0.2752
	0.2222	0.2021	0.0760	0.3573	0.1424	0.3329	0.2796	0.0957	0.2390	0.0528	0.0494	0.0764	0.0487	0.5477	0.2778
	0.2096	0.1904	0.1004	0.3573	0.1423	0.2927	0.2499	0.1250	0.2666	0.0658	0.0443	0.0668	0.0592	0.5403	0.2894
0.3085	0.2633	0.2376	0.0000	0.3446	0.1545	0.4817	0.3852	0.0000	0.1173	0.0158	0.0316	0.0676	0.0000	0.6030	0.2978
	0.2493	0.2263	0.0255	0.3445	0.1544	0.4380	0.3539	0.0335	0.1518	0.0228	0.0334	0.0665	0.0157	0.5838	0.3006
	0.2358	0.2141	0.0503	0.3451	0.1547	0.3935	0.3236	0.0671	0.1837	0.0321	0.0352	0.0633	0.0293	0.5627	0.3095
	0.2231	0.2019	0.0752	0.3451	0.1547	0.3473	0.2882	0.0989	0.2192	0.0464	0.0354	0.0588	0.0413	0.5454	0.3191
	0.2097	0.1904	0.1003	0.3431	0.1565	0.3027	0.2542	0.1287	0.2522	0.0622	0.0326	0.0519	0.0502	0.5240	0.3413
0.3357	0.2614	0.2376	0.0000	0.3329	0.1681	0.4869	0.4006	0.0000	0.0996	0.0129	0.0191	0.0481	0.0000	0.5929	0.3399
	0.2486	0.2260	0.0256	0.3320	0.1678	0.4420	0.3694	0.0365	0.1315	0.0206	0.0206	0.0472	0.0129	0.5729	0.3464
	0.2365	0.2139	0.0501	0.3319	0.1676	0.4036	0.3361	0.0714	0.1613	0.0276	0.0212	0.0435	0.0235	0.5537	0.3581
	0.2220	0.2013	0.0747	0.3335	0.1685	0.3579	0.3025	0.1048	0.1955	0.0393	0.0174	0.0391	0.0325	0.5464	0.3646
	0.2088	0.1896	0.0996	0.3335	0.1685	0.3172	0.2695	0.1361	0.2258	0.0514	0.0186	0.0346	0.0386	0.5245	0.3837
	0.1966	0.1785	0.1252	0.3320	0.1677	0.2841	0.2499	0.1618	0.2465	0.0577	0.0146	0.0283	0.0428	0.5179	0.3964
0.4215	0.2621	0.2378	0.0000	0.2893	0.2108	0.4921	0.4156	0.0000	0.0818	0.0105	0.0075	0.0240	0.0000	0.5442	0.4243
	0.2487	0.2262	0.0252	0.2892	0.2107	0.4522	0.3855	0.0393	0.1082	0.0148	0.0081	0.0223	0.0078	0.5111	0.4507
	0.2343	0.2131	0.0500	0.2907	0.2119	0.4121	0.3558	0.0788	0.1310	0.0223	0.0076	0.0199	0.0140	0.5010	0.4575
	0.2228	0.2020	0.0750	0.2893	0.2109	0.3722	0.3222	0.1155	0.1613	0.0288	0.0066	0.0173	0.0185	0.4896	0.4680
	0.2097	0.1905	0.1001	0.2891	0.2106	0.3349	0.2931	0.1527	0.1833	0.0360	0.0046	0.0137	0.0216	0.4889	0.4712
	0.1831	0.1663	0.1502	0.2895	0.2109	0.2725	0.2374	0.2162	0.2225	0.0514	0.0033	0.0083	0.0221	0.4629	0.5034
	0.1837	0.1671	0.1500	0.2888	0.2104	0.2708	0.2396	0.2181	0.2186	0.0529	0.0034	0.0089	0.0229	0.4536	0.5112

[a] w_{5S}= water mass fraction in the alcoholic solvent.

Table 3. UNIQUAC and NRTL Parameters at (298.2 ± 0.1) K

	UNIQUAC model		NRTL model		
pair ij[a]	A_{ij}/K	A_{ji}/K	A_{ij}/K	A_{ji}/K	α_{ij}
12	−69.127	−119.15	−489.47	2000.00	0.36
13	814.28	−373.47	−1072.30	11.74	0.16
14	377.19	−110.45	−597.93	1189.70	0.19
15	510.83	280.37	−0.13	2932.40	0.18
23	109.35	16.04	−868.05	3873.90	0.43
24	285.95	−260.98	135.34	105.92	0.10
25	505.98	265.92	1819.90	2931.00	0.16
34	171.57	−112.69	−1176.20	157.97	0.20
35	−16.04	5000.00	44.88	2129.50	0.20
45	295.73	−184.56	−319.87	512.25	0.37

[a] Limonene (1), linalyl acetate (2), linalool (3), ethanol (4), and water (5).

Table 4. Mean Deviations between the Experimental and Calculated Compositions in Both Phases

	Δw[a]	
w_{5S}	UNIQUAC	NRTL
0.2849	0.0027	0.0062
0.3095	0.0041	0.0060
0.3357	0.0035	0.0051
0.4215	0.0056	0.0039
global deviation of the correlation	0.0043	0.0052

[a] Calculated according to eq 8.

(ethanol plus water) at (298.2 ± 0.1) K were obtained and correlated on the basis of the NRTL and UNIQUAC equations.

Table 1 presents CAS registry numbers and experimental purities of compounds, the molar masses, values of the volume, and area parameters that were calculated using eq 6.

In Table 2, the overall phase compositions and the corresponding tie lines for the quinary model systems composed of limonene (1), linalyl acetate (2), linalool (3), ethanol (4), and water (5) at (298.2 ± 0.1) K are shown. All compositions are given as mass fractions.

The adjusted parameters of the NRTL and UNIQUAC models are shown in Table 3. Mean deviations between experimental and calculated compositions in both phases are shown in Table 4.

Figures 1 and 2 show experimental and calculated limonene (k_1) and linalyl acetate (k_2) distribution coefficients and linalyl acetate/limonene ($S_{2/1}$) selectivities as a function of the linalool mass fraction in the terpene phase (w_3^{TP}). These figures present the corresponding results for each water mass fraction in the solvent (0.2849 and 0.3085 in Figure 1, 0.3357 and 0.4215 in Figure 2).

The distribution coefficients were calculated according to eq 9, while the selectivities were calculated as described below (eq 12).

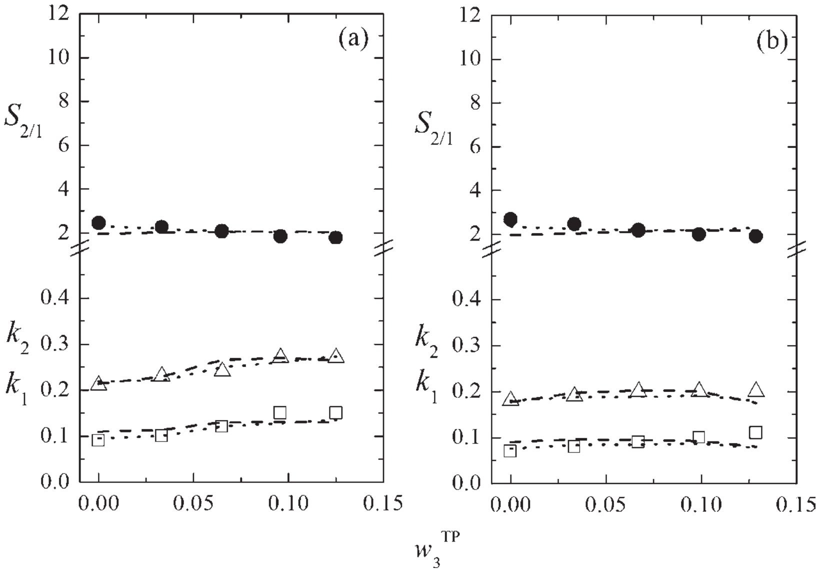

Figure 1. Distribution coefficients of limonene (k_1) and linalyl acetate (k_2), and linalyl acetate/limonene selectivity ($S_{2/1}$), at (298.2 ± 0.1) K, for the systems composed of limonene (1) + linalyl acetate (2) + linalool (3) + ethanol (4) + water (5). Experimental: □, k_1; Δ, k_2; ●, $S_{2/1}$. Calculated: ---, NRTL; ···, UNIQUAC. (a) w_{5S} = 0.2849; (b) w_{5S} = 0.3085.

$$S_{i/j} = \frac{k_i}{k_j} \tag{12}$$

The linalool (k_3) distribution coefficients as well as the linalool/limonene ($S_{3/1}$) and linalool/linalyl acetate ($S_{3/2}$) selectivities are shown in Figures 3 and 4. Similar to Figures 1 and 2, these corresponding values were also plotted against the linalool mass fraction in the terpene phase (w_3^{TP}).

The results shown in Figures 1−4 indicate that both thermodynamic models provided a good representation of the compounds distribution between the two liquid phases but that the UNIQUAC model provided a better estimation of limonene, linalyl acetate, and linalool compositions (see global deviations in Table 4).

From the data presented in Figures 1−4, it can be observed that the increase in water mass fractions in the alcoholic solvent reduced the solvent's capacity to extract terpene hydrocarbon (limonene), terpene ester (linalyl acetate), and terpene alcohol (linalool). In fact, this effect is probably due to a reduction in mutual solubility among the components of the system.

In Figures 1−4, it can also be observed that the linalool distribution coefficient was always higher compared to that of limonene and linalyl acetate and that, between these last two components, linalyl acetate presented higher *k* values. In fact, these values denote the solvent affinity by the compound, showing a higher distribution coefficient for the components of higher polarity; these coefficients can be listed in ascending order as limonene, linalyl acetate, and linalool.

It can also be observed that the addition of water caused a significant increase in solvent selectivity and that the linalool/limonene selectivity ($S_{3/1}$) values were always the highest compared to the linalyl acetate/limonene ($S_{2/1}$) and linalool/linalyl acetate ($S_{3/2}$) selectivities, indicating a high solvent affinity by linalool.

In general, our results of the distribution coefficients and selectivities are in agreement with previous results published by Arce et al.[33] These authors reported the liquid−liquid equilibrium for systems containing limonene, linalool, ethanol, and water at 298.15 K.

The data presented in Table 2 corroborate previous observations regarding the effect of water level in the solvent on the distribution coefficients. By evaluating those tie lines containing linalool mass fraction around 0.0250 in the overall composition, it is possible to observe that, for all kinds of alcoholic solvents studied, limonene, linalyl acetate, and linalool present a decrease in distribution coefficient values of 80, 74, and 62%, respectively. The aforementioned figures indicate that the reduction in the distribution coefficient seems to be not proportionally equal for the components, because limonene was the most affected followed by linalyl acetate and then linalool. This effect can be related to the chemical affinity between water and other components in the system, where the small effects are related to compounds of higher polarity.

To investigate the effect of process variables (water mass fraction in the solvent, w_{5S}, and the linalool mass fraction in the terpene phase, w_3^{TP}) on the distribution coefficients of the essential oil compounds, complete second-order models, eqs 13−15, were fitted to the experimental data as previously described.

$$k_1 = 1.27 - 6.48w_{5S} + 8.35(w_{5S})^2 + 1.26w_3^{TP} - 0.40(w_3^{TP})^2 - 2.89w_3^{TP}w_{5S} \tag{13}$$

$$k_2 = 1.95 - 9.29w_{5S} + 11.39(w_{5S})^2 + 1.09w_3^{TP} - 0.95(w_3^{TP})^2 - 2.38w_3^{TP}w_{5S} \tag{14}$$

$$k_3 = 2.85 - 11.70w_{5S} + 12.94(w_{5S})^2 - 1.18w_3^{TP} - 0.51(w_3^{TP})^2 + 1.82w_3^{TP}w_{5S} \tag{15}$$

where w_{5S} and w_3^{TP} represent water mass fraction in the solvent and linalool mass fraction in the terpene phase, respectively.

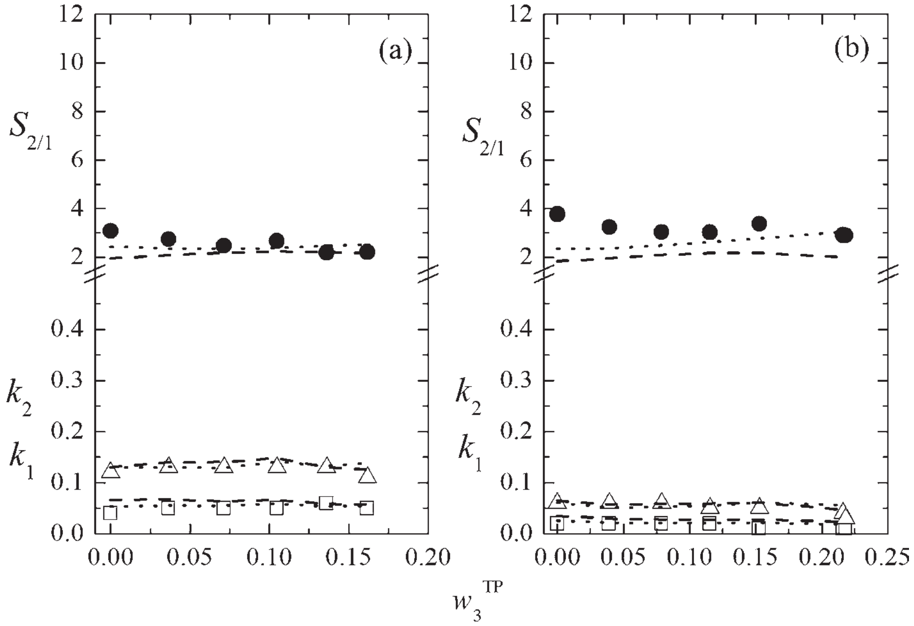

Figure 2. Distribution coefficients of limonene (k_1) and linalyl acetate (k_2), and linalyl acetate/limonene selectivity ($S_{2/1}$), at (298.2 ± 0.1) K, for the systems composed of limonene (1) + linalyl acetate (2) + linalool (3) + ethanol (4) + water (5). Experimental: □, k_1; Δ, k_2; ●, $S_{2/1}$. Calculated: ---, NRTL; · · ·, UNIQUAC. (a) w_{5S} = 0.3357; (b) w_{5S} = 0.4215.

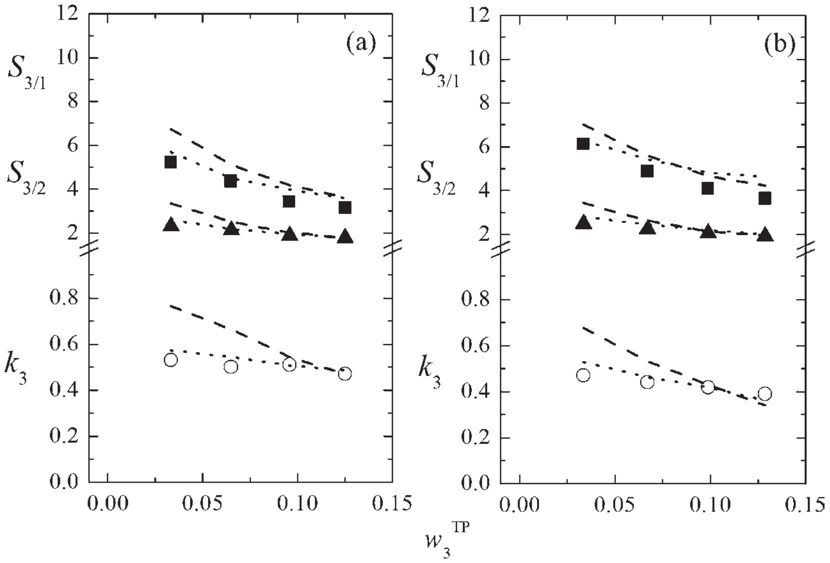

Figure 3. Distribution coefficient of linalool (k_3), and linalool/limonene ($S_{3/1}$), and linalool/linalyl acetate ($S_{3/2}$) selectivities, at (298.2 ± 0.1) K, for the systems composed of limonene (1) + linalyl acetate (2) + linalool (3) + ethanol (4) + water (5). Experimental: ○, k_3; ■, $S_{3/1}$; ▲, $S_{3/2}$. Calculated: −−−, NRTL; · · ·, UNIQUAC. (a) w_{5S} = 0.2849; (b) w_{5S} = 0.3085.

Table 5 presents the analysis of variance (ANOVA) for these adjusted models at 0.95 confidence. The three fitted models presented high correlation coefficients and acceptable ARD values (calculated between the experimental values and those estimated using the adjusted second-order equations, eq 11). Additionally, in the *F*-test, the calculated *F*-values indicate that the models were reliable. As a practical rule, a model is statistically significant when the calculated *F*-value is at least 3−5 times greater than the listed value.[50]

On the basis of these statistical models (eqs 13 to 15), contour curves were produced using Origin Software (OriginLab, version 8.0). These contour curves represent the influence of independent variables, w_{5S} and w_3^{TP}, on the distribution coefficients of the essential oil compounds (Figures 5−7).

In Figures 5−7, it can be observed that the behavior of the distribution coefficients was different. In fact, it is possible to observe that an increase in solvent water content caused a reduction in the *k* value, regardless of the compound studied. This observation supports the previous comments regarding the lower extracting capacity with higher water content in the ethanol (see Figures 1−4).

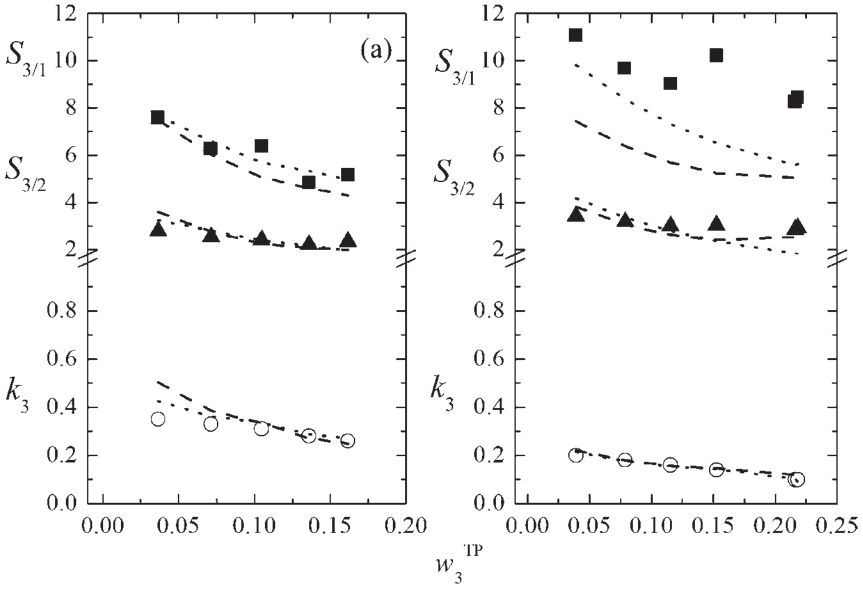

Figure 4. Distribution coefficient of linalool (k_3), and linalool/limonene ($S_{3/1}$), and linalool/linalyl acetate ($S_{3/2}$) selectivities, at (298.2 ± 0.1) K, for the systems composed of limonene (1) + linalyl acetate (2) + linalool (3) + ethanol (4) + water (5). Experimental: ○, k_3; ■, $S_{3/1}$; ▲, $S_{3/2}$. Calculated: ———, NRTL; · · ·, UNIQUAC. (a) w_{5S} = 0.3357; (b) w_{5S} = 0.4215.

Table 5. Analysis of Variance (ANOVA)

	k_1				k_2				k_3			
source of variation	SS[a]	MS[b]	DF[c]	F value[d]	SS	MS	DF	F value[e]	SS	MS	DF	F value[f]
regression	0.040	0.0081	5	118.50	0.129	0.026	5	228.54	0.376	0.075	5	606.21
residual	0.0012	6.8×10^{-5}	17		0.0019	1.13×10^{-4}	17		0.0016	1.24×10^{-4}	13	
total	0.041		22		0.131		22		0.378		18	
correlation coefficient	0.99				0.99				0.99			
ARD[g]	0.1128				0.0549				0.0194			

[a] Sum of squares. [b] Mean square. [c] Degrees of freedom. [d] F calc = $F_{0.95;5;17}$ = 2.81. [e] F calc = $F_{0.95;5;17}$ = 2.81. [f] F calc = $F_{0.95;5;13}$ = 3.03. [g] Average relative deviation calculated according to eq 11.

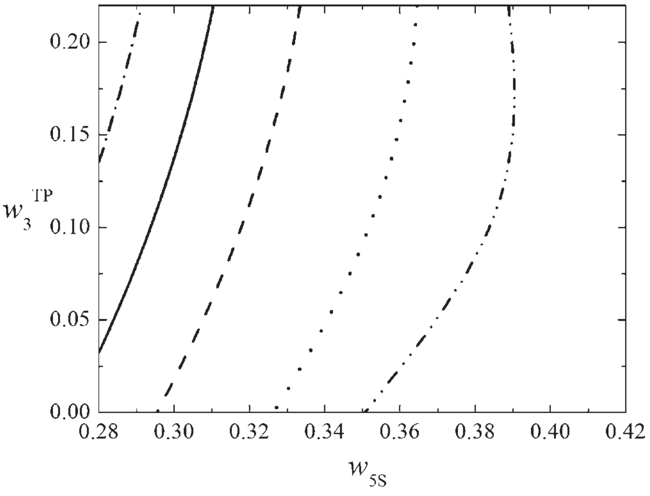

Figure 5. Contour curves of limonene distribution coefficient (k_1) expressed as a function of water mass fraction in the solvent, w_{5S}, and linalool mass fraction in the terpene phase, w_3^{TP}. Calculated: —·—, k_1 = 0.20; —, k_1 = 0.10; ———, k_1 = 0.080; · · ·, k_1 = 0.040; —· · ·—, k_1 = 0.020.

Conversely, the effect of higher linalool content in the terpenic phase on the distribution coefficient is more prominent for limonene than for linalyl acetate.

In Figures 5 and 6, it can be observed that as the linalool content increased, the hydrocarbon terpene and ester distribution coefficients increased. However, the linalool distribution coefficient values were negatively affected by the alcohol level on the terpene phase (see Figure 7).

This analysis can help to optimize the deterpenation process using countercurrent liquid–liquid extraction columns.

■ CONCLUSIONS

The results presented in this paper help to improve the essential oil deterpenation process by liquid–liquid extraction, and knowledge of the distribution coefficient of the compounds as well as the solvent selectivity is extremely important for the proper design of liquid–liquid extractors.

The compositions of the solvent and terpenic phases were well represented by the estimated parameters of the NRTL and UNIQUAC models, as the descriptions of the liquid–liquid

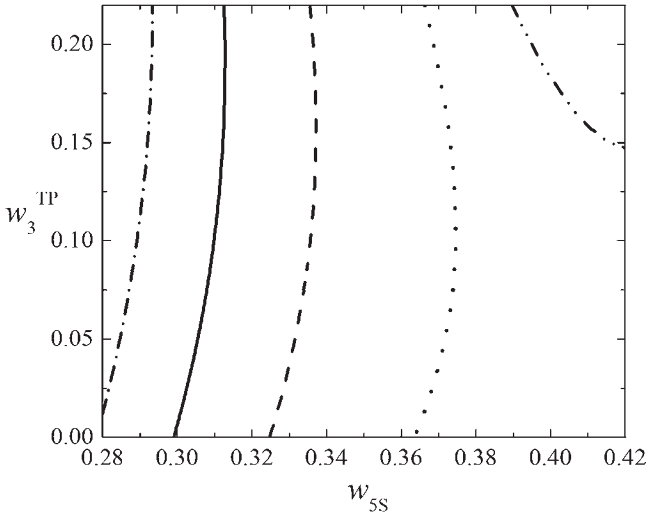

Figure 6. Contour curves of linalyl acetate distribution coefficient (k_2) expressed as a function of water mass fraction in the solvent, w_{5S}, and linalool mass fraction in the terpene phase, w_3^{TP}. Calculated: —•—, k_2 = 0.24; —, k_2 = 0.19; – – –, k_2 = 0.13; • • •, k_2 = 0.076; —• • —, k_2 = 0.048.

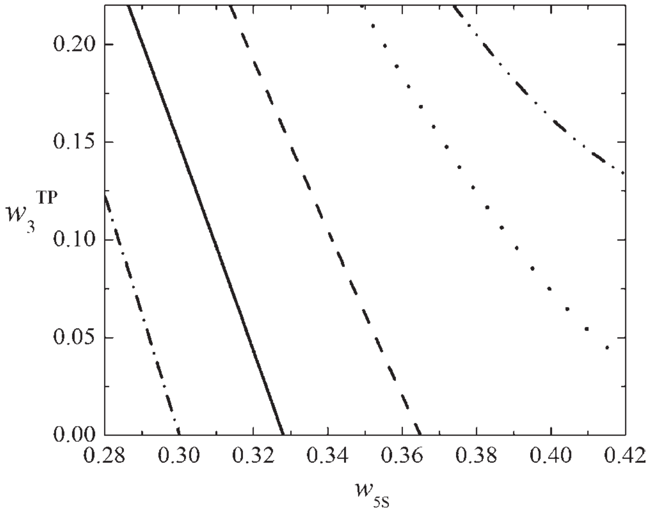

Figure 7. Contour curves of linalool distribution coefficient (k_3) expressed as a function of water mass fraction in the solvent, w_{5S}, and linalool mass fraction in the terpene phase, w_3^{TP}. Calculated: —•—, k_3 = 0.50; —, k_3 = 0.40; – – –, k_3 = 0.30; • • •, k_3 = 0.20; —• • —, k_3 = 0.15.

equilibrium for all the systems presented mean deviations lower than 0.0062 compared to the experimental data.

The UNIQUAC model provided a better description of the experimental compositions compared to NRTL. However, it is possible to model and simulate liquid—liquid extractors for essential oils deterpenation using both models.

Second-order models were used to evaluate the essential oil compound distribution coefficients at different conditions of water mass fraction in the solvent and the linalool mass fraction in the terpene phase. On the basis of these statistical models, it was observed that a higher water content in the solvent phase resulted in a lower k value, regardless of compound type. Conversely, a higher linalool content promoted an increase in the distribution coefficients of hydrocarbon terpene and ester. Regarding the linalool distribution coefficients, it was observed that these values were negatively affected by the terpene alcohol level in the terpene phase. This information is useful to optimize the deterpenation process using liquid—liquid extraction.

■ AUTHOR INFORMATION

Corresponding Author

*Fax: + 55-19-3565-4343. E-mail: chrisrodrigues@usp.br.

Funding Sources

We acknowledge FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo, 2006/05973-3, 2008/07326-0, 2009/07910-7, 2009/17271-1), CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico), and CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior) for the financial support.

■ REFERENCES

(1) Cháfer, A.; de la Torre, J.; Muñoz, R.; Burguet, M. C. Liquid-Liquid Equilibria of the Mixture Linalool + Ethanol + Water at Different Temperatures. *Fluid Phase Equilib.* **2005**, *238*, 72–76.

(2) http://comtrade.un.org/db (accessed June 25, 2010).

(3) Gironi, F.; Maschietti, M. Continuous Countercurrent Deterpenation of Lemon Essential Oil by Means of Supercritical Carbon Dioxide: Experimental Data and Process Modeling. *Chem. Eng. Sci.* **2008**, *63*, 651–661.

(4) Gattuso, G.; Barreca, D.; Caristi, C.; Gargiulli, C.; Leuzzifantin, U. Distribution of Flavonoids and Furocoumarins in Juices from Cultivars of *Citrus bergamia* Risso. *J. Agric. Food Chem.* **2007**, *55*, 9921–9927.

(5) Franceschi, E.; Grings, M. B.; Frizzo, C. D.; Oliveira, J. V.; Dariva, C. Phase behavior of lemon and bergamot peel oils in supercritical CO_2. *Fluid Phase Equilib.* **2004**, *226*, 1–8.

(6) Fantin, G.; Fogagnolo, M.; Maietti, S.; Rossetti, S. Selective Removal of Monoterpenes from Bergamot Oil by Inclusion in Deoxycholic Acid. *J. Agric. Food Chem.* **2010**, *58*, 5438–5443.

(7) Varona, S.; Martin, A.; Cocero, M. J.; Gamse, T. Supercritical Carbon Dioxide Fractionation of Lavandin Essential Oil: Experiments and Modeling. *J. Supercrit. Fluids* **2008**, *45*, 181–188.

(8) Raeissi, S.; Diaz, S.; Espinosa, S.; Peters, C. J.; Brignole, E. A. Ethane As An Alternative Solvent for Supercritical Extraction of Orange Peel Oils. *J. Supercrit. Fluids* **2008**, *45*, 306–313.

(9) Molina, C.; Steinchen, A.; Charbit, G.; Charbit, F. Model for pervaporation: application to ethanolic solutions of aroma. *J. Membr. Sci.* **1997**, *132*, 119–129.

(10) Figoli, A.; Tagarelli, A.; Mecchia, A.; Trotta, A.; Cavaliere, B.; Lavecchia, R.; Sindona, G.; Drioli, E. Enzyme-assisted pervaporative recovery of concentrated bergamot peel oils. *Desalination* **2006**, *199*, 111–112.

(11) Reverchon, E. Supercritical Desorption of Limonene and Linalool from Silica Gel: Experiments and Modelling. *Chem. Eng. Sci.* **1997**, *52*, 1019–1027.

(12) Danielski, L.; Brunner, G.; Schwänke, C.; Zetzl, C.; Hense, H.; Donoso, J. P. M. Deterpenation of mandarin (*Citrus reticulata*) peel oils by means of countercurrent multistage extraction and adsorption/desorption with supercritical CO_2. *J. Supercrit. Fluids* **2008**, *44*, 315–324.

(13) Rouatbi, M.; Duquenoy, A.; Giampaoli, P. Extraction of the essential oil of thyme and black pepper by superheated steam. *J. Food Eng.* **2007**, *78*, 708–714.

(14) Stuart, G. R.; Lopes, D.; Oliveira, J. V. Deterpenation of Brazilian Orange Peel Oil by Vacuum Distillation. *J. Am. Oil Chem. Soc.* **2001**, *78*, 1041–1044.

(15) Paroul, N.; Biasi, A.; Rovani, A. C.; Prigol, C.; Dallago, R.; Treichel, H.; Cansian, R. L.; Oliveira, J. V.; Oliveira, D. Enzymatic Production of Linalool Esters in Organic and Solvent-Free System. *Bioprocess Biosyst. Eng.* **2010**, *33*, 583–589.

(16) Rottava, I.; Toniazzo, G.; Cortina, P. F.; Martello, E.; Grando, C. E.; Lerin, L. A.; Treichel, H.; Mossi, A. J.; Oliveira, D.; Cansian, R. L.; Antunes, O. A. C.; Oestreicher, E. G. Screening of Microorganisms for Bioconversion of (-)β-Pinene and R-(+)-Limonene to α-Terpineol. *LWT-Food Sci. Technol.* **2010**, *43*, 1128–1131.

(17) Arce, A.; Marchiaro, A.; Rodríguez, O.; Soto, A. Essential Oil Terpenless by Extraction Using Organic Solvents or Ionic Liquids. *AIChE J.* **2006**, *52*, 2089–2097.

(18) Gramajo de Doz, M. B.; Cases, A. M.; Díaz, Pablo A.; Sólimo, H. N. (Liquid + Liquid) Equilibria for Water + Ethanol + Citral Multicomponent System at 303.15 K. *J. Chem. Eng. Data* **2007**, *52*, 1710–1714.

(19) Tamura, K.; Li, H. Mutual Solubilities of Terpene in Methanol and Water and Their Multicomponent Liquid-Liquid Equilibria. *J. Chem. Eng. Data* **2005**, *50*, 2013–2018.

(20) Rodrigues, C. E. C.; Peixoto, E. C. D.; Meirelles, A. J. A. Phase Equilibrium for Systems Composed by Refined Soybean Oil + Commercial Linoleic Acid + Ethanol + Water, at 323.2K. *Fluid Phase Equilib.* **2007**, *261*, 122–128.

(21) Arce, A.; Pobudkowska, A.; Rodríguez, O.; Soto, A. Citrus Essential Oil Terpenless by Extraction Using 1-Ethyl-3-Methylimidazolium Ethylsulfate Ionic Liquid: Effect of the Temperature. *Chem. Eng. J.* **2007**, *133*, 213–218.

(22) Arce, A.; Marchiaro, A.; Rodríguez, O.; Soto, A. Liquid-Liquid Equilibria of Limonene + Linalool + Diethylene Glycol System at Different Temperaturas. *Chem. Eng. J.* **2002**, *89*, 223–227.

(23) Arce, A.; Marchiaro, A.; Soto, A. Propanediols for Separation of Citrus Oil: Liquid-Liquid Equilibria of Limonene + Linalool + (1,2-Propanediol or 1,3-Propanediol). *Fluid Phase Equilib.* **2003**, *211*, 129–140.

(24) Sevgili, L. M.; Sahin, S.; Kirbaslar, S. I. Liquid-Liquid Equilibria of (Limonene + Linalool + Ethylene Glycol or Diethylene Glycol or Triethylene Glycol or 1,2-Propylene Glycol) Ternary Systems. *J. Chem. Eng. Data* **2008**, *53*, 737–741.

(25) Gramajo de Doz, M. B.; Cases, A. M.; Sólimo, H. N. (Liquid + Liquid) Equilibria for (Water + Linalol + Limonene) Ternary System at T = (298.15, 308.15 and 318.15) K. *J. Chem. Thermodyn.* **2008**, *112*, 1575–1579.

(26) Arce, A.; Marchiaro, A.; Soto, A. Liquid-Liquid Equilibria of Linalool + Ethanol + Water, Water + Ethanol + Limonene, and Limonene + Linalool + Water Systems. *J. Solution Chem.* **2004**, *33*, 561–569.

(27) Arce, A.; Marchiaro, A.; Soto, A. Phase Stability of the System Limonene + Linalool + 2-Aminoethanol. *Fluid Phase Equilib.* **2004**, *226*, 121–127.

(28) Antosik, M.; Stryjek, R. Liquid-Liquid Equilibria In Ternary α-Pinene + Δ3-Carene + Polar Compound Systems. *Fluid Phase Equilib.* **1992**, *71*, 321–331.

(29) Tamura, K.; Li, X.; Li, H. Temperature Dependence on Mutual Solubility Data of the Binary (Methanol +α-Pinene or β-Pinene) Systems and Ternary Liquid-Liquid Equilibria for the (Methanol + Ethanol + α-Pinene or β-Pinene) Systems. *J. Chem. Eng. Data* **2008**, *53*, 2417–2421.

(30) Tamura, K.; Li, X.; Li, H. Temperature Dependence on Mutual Solubility of Binary (Methanol + Limonene) Mixture and (Liquid-Liquid) Equilibria of the Ternary (Methanol + Ethanol + Limonene) Mixture. *J. Chem. Thermodyn.* **2009**, *41*, 564–568.

(31) Gironi, F.; Farias, I. G.; Lamberti, L. Liquid-Liquid Equilibria for the Water + Ethanol + Citral and Water + Ethanol + Limonene Systems at 293 K. *J. Chem. Eng. Data* **1995**, *40*, 578–581.

(32) Cháfer, A.; Muñoz, R.; Burguet, M. C.; Berna, A. The Influence of the Temperature on the Liquid-Liquid Equilibria of the Mixture Linalool + Ethanol + H_2O. *Fluid Phase Equilib.* **2004**, *224*, 251–256.

(33) Arce, A.; Marchiaro, A.; Martínez-Ageitos, J. M.; Soto, A. Citrus Essential Oil Deterpenation by Liquid-Liquid Extraction. *Can. J. Chem. Eng.* **2005**, *83*, 366–370.

(34) Li, H.; Tamura, K. Ternary and Quaternary (Liquid + Liquid) Equilibria for (Water + Ethanol + α-Pinene, +β-Pinene, or +Limonene) and (Water + Ethanol + α-Pinene + Limonene) at the Temperature 298.15 K. *J. Chem. Thermodyn.* **2006**, *38*, 1036–1041.

(35) Li, H.; Tamura, K. Ternary Liquid−Liquid Equilibria for (Water + Terpene + 1-Propanol or 1-Butanol) Systems at the Temperature 298.15 K. *Fluid Phase Equilib.* **2008**, *263*, 223–230.

(36) Renon, H.; Prausnitz, J. M. Liquid-liquid and vapor-liquid equilibria for binary and ternary systems with dibutyl ketone dimethyl sulfoxide n-hexane and 1-hexene. *Ind. Eng. Chem. Process Des. Dev.* **1968**, *7*, 220–225.

(37) Abrams, D. S.; Prausnitz, J. M. Statistical thermodynamics of liquid mixtures: a new expression for the excess gibbs energy of partly or completely miscible systems. *AIChE J.* **1975**, *21*, 116–128.

(38) Rodrigues, C. E. C.; Antoniassi, R.; Meirelles, A. J. A. Equilibrium Data for the System Rice Bran Oil + Fatty Acids + Ethanol + Water at 298.2 K. *J. Chem. Eng. Data* **2003**, *48*, 367–373.

(39) Taylor, B. N.; Kuyatt, C. E. *Guidelines for the Evaluation and Expression of Uncertainty in NIST Measurement Results*; NIST Technical Note 1297; NIST: Gaithersburg, MD, 1994.

(40) Marcilla, A.; Ruiz, F.; García, A. N. Liquid-Liquid-Solid Equilibria of the Quaternary System Water − Ethanol − Acetone − Sodium Chloride at 25 °C. *Fluid Phase Equilib.* **1995**, *112*, 273–289.

(41) Rodrigues, C. E. C.; Reipert, E. C. C. D.; Souza, A. F.; Pessôa Filho., P. A.; Meirelles, A. J. A. Equilibrium Data for Systems Composed by Cottonseed Oil + Commercial Linoleic Acid + Ethanol + Water + Tocopherols at 298.2 K. *Fluid Phase Equilib.* **2005**, *238*, 193–203.

(42) Gonçalves, C. B.; Batista, E.; Meirelles, A. J. A. Liquid-Liquid Equilibrium Data for the System Corn Oil + Oleic Acid + Ethanol + Water at 298.15 K. *J. Chem. Eng. Data* **2002**, *47*, 416–420.

(43) Gonçalves, C. B.; Meirelles, A. J. A. Liquid-Liquid Equilibrium Data for the System Palm Oil + Fatty Acids + Ethanol + Water at 318.2 K. *Fluid Phase Equilib.* **2004**, *221*, 139–150.

(44) Rodrigues, C. E. C.; Meirelles, A. J. A. Extraction of Free Fatty Acids from Peanut Oil and Avocado Seed Oil: Liquid-Liquid Equilibrium Data at 298.2 K. *J. Chem. Eng. Data* **2008**, *53*, 1698–1704.

(45) Lanza, M.; Borges Neto, W.; Batista, E.; Poppi, R. J.; Meirelles, A. J. A. Mutual Solubility of Pseudobinary Systems Containing Vegetable Oils and Anhydrous Ethanol from (298.15 to 333.15) K. *J. Chem. Eng. Data* **2008**, *53*, 5–15.

(46) Cuevas, M. S.; Rodrigues, C. E. C.; Meirelles, A. J. A. J. Effect of Solvent Hydration and Temperature in the Deacidification Process of Sunflower Oil Using Ethanol. *J. Food Eng.* **2009**, *95*, 291–297.

(47) Rodrigues, C. E. C.; Pessôa Filho, P. A.; Meirelles, A. J. A. Phase Equilibrium for the System Rice Bran Oil + Fatty Acids + Ethanol + Water + γ-Oryzanol + Tocols. *Fluid Phase Equilib.* **2004**, *216:2*, 271–283.

(48) Magnussen, T.; Rasmussen, P.; Fredenslund, A. Unifac Parameter Table for Prediction of Liquid-Liquid Equilibria. *Ind. Eng. Chem. Process Des. Dev.* **1981**, *20*, 331–339.

(49) Stragevitch, L.; d'Avila, S. G. Application of a Generalized Maximum Likelihood Method in the Reduction of Multicomponent Liquid- Liquid Equilibrium Data. *Braz. J. Chem. Eng.* **1997**, *14*, 41–52.

(50) Box, G. E. P.; Hunter, W. G.; Hunter, J. S. *Statistic for Experimenters − An Introduction to Design, Data Analysis and Model Building*; John Wiley & Sons: New York, 1978.