J. Chem. Eng. Data **2001,** *46,* 1145−1148

High Pressure Solubility Data of the System Limonene + Linalool + CO_2

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The feasibility of deterpenating orange peel oil with supercritical CO_2 depends on relevant vapor−liquid equilibrium data because the selectivity of this solvent for limonene and linalool (the two key components of the oil) is of crucial importance. In this work the solubility data for the CO_2 + limonene + linalool ternary system were measured at (318.2 and 328.2) K. The range of pressures covered was from (70 to 110) bar. Two different mixtures of limonene + linalool were used: a 40 mass % limonene + 60 mass % linalool mixture and a 60 mass % limonene + 40 mass % linalool mixture. To correlate the obtained results, two equations of state were successfully used (Peng−Robinson (PR) and Soave−Redlich−Kwong (SRK)).

Introduction

Citrus oil is present in the flavedo, which is the colored portion of the peel of oranges and other fruits. It is a useful raw material for the food and perfumery industries. Cold-pressed oil is recovered by pressure or abrasion before or during juice extraction followed by a subsequent centrifuge operation.

More than 200 compounds have been identified in cold-pressed orange oil. These compounds can be grouped into the following two fractions: (a) The terpene fraction involves approximately 95 mass % of the orange oil. The major component is D-limonene, which is an unsaturated terpene hydrocarbon of 10 atoms of carbon. (b) The flavor fraction is composed of different oxygenated compounds such as aldehydes, alcohols, esters, and ketones, which give the characteristic citrus flavor. The most representative compound of this fraction, which is difficult to separate from the terpene fraction, is linalool.

Limonene is unstable to heat, light, and oxygen. So, it is common industrial practice to remove limonene and other terpenes to concentrate the oxygenated compounds such as linalool.[1] Vacuum distillation, steam distillation, extraction with solvents, and desorption are the current processes for concentrating the cold-pressed oils. The drawbacks of all these processes are low yields, formation of degradation products, and/or addition of an extracting solvent that must be removed. Furthermore, it must be considered that the unsaturated terpene hydrocarbon degrades to undesired products.

Supercritical carbon dioxide extraction appears to be an alternative process for concentrating because it offers the advantages of low operating temperature and no solvent residue.[2,3]

The basic principles of supercritical fluid extraction have been reviewed previously.[4−10]

As a first approximation, orange peel oil can be considered a binary mixture of its two key compounds, limonene and linalool, representing the terpene and the oxygenated fractions, respectively.[3,11] Vapor−liquid equilibrium data are required for the mixture of CO_2 + limonene + linalool, to design a supercritical fluid separation unit. The binary solubility data for CO_2 + limonene and for CO_2 + linalool were measured and reported in previous works[12] at (318.2 and 328.2) K and a pressure range of (69−111) bar. Other binary equilibrium data can be found in the literature.[10,13−20] Some authors had tried to perform supercritical deterpenation simulation of the mixture limonene + linalool or the cold-pressed orange oil, taking as a basis these binary data.[3,11,21,22] On the other hand, Vieira de Melo et al.[20] concluded that the selectivity calculated directly from the ternary VLE data for limonene + linalool + CO_2 are smaller than those from the binary VLE data. This fact suggests that molecular interaction between limonene and linalool cannot be neglected because accurate thermodynamic modeling of this kind of behavior is crucial in a developing separation process. So, it is necessary to have an extended data set of the ternary system for a reliable simulation of industrial application. There are available some literature data of the ternary system,[20,23] but the range of temperature and pressures is small and, for the vapor phase, they are concentrated in the pure CO_2 vertex of the ternary diagram phase. So, for an accurate simulation of the process, it is necessary to extend the experimental data range.

In this work the solubility data for the CO_2 + limonene + linalool ternary system were measured at (318.2 and 328.2) K. The range of pressures covered was from (70 to 110) bar. Finally, two different mixtures of limonene + linalool were used: a 40 mass % limonene + 60 mass % linalool mixture and a 60 mass % limonene + 40 mass % linalool mixture. Like this, the range of the experimental data set was widely extended.

Experimental Section

Chemicals. Limonene and linalool (99 mass %, GC grade) were purchased from Aldrich Chemical Co., Inc. Dichloromethane (99.9 mass %, GC grade) supplied by Scharlau Chimie S.A. was used as modifier and solvent to

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10.1021/je010029y CCC: \$20.00

collect the extract. The reagents were used without further purification after chromatography failed to show any significant impurities. High-purity CO_2 (more than 99.9 vol % purity, SFC grade) was used as received. Diatomaceous earth calcined, extra pure (Scharlau Chimie S.A.), was utilized as support of products.

Equipment and Procedure. Solubilities were measured with an SFX 3560 extractor with two Model 260D syringe pumps manufactured by ISCO (Lincoln, NE). This equipment was described in a previous paper (Berna et al.[26]). With the proper plumbing, a two-pump system can deliver continuous flow of supercritical fluid. A modifier can be added. The cylinder capacity of the pump is 266 mL and the maximum pressure 510 bar. The temperature can range from 313.2 K to 423.2 K, and supercritical fluid flow can range between 0.5 mL/min and 5 mL/min. The SFX 3560 sample reel holds up to 24 sample cartridges (10 mL) and collection vials.

The extractor measured the amount of supercritical CO_2 used in extraction. The flow of supercritical fluid used for all experiments was 2 mL/min. This value allows us to minimize the residence time and obtain saturation of the fluid. Dichloromethane was used to trap the limonene and linalool extracted. After that, the extract was transferred to 10 mL calibrated flasks and diluted with dichloromethane. In some cases, a higher dilution could be necessary to achieve a concentration level adequate for supercritical chromatography determination.

For sample preparation, 0.6 g of diatomaceous earth was weighed and placed in the sample cartridge. Then, a volume of (200−400) μL of product (a mixture of limonene and linalool) was added to diatomaceous earth in the cartridge. The role of this material is to avoid the draining of the liquid.

The compositions of the extract samples were determined using a Hewlett-Packard 5890 S−II gas chromatograph (GC), after calibration with gravimetrically prepared standard solutions. A flame ionization detector was used together with a 60 m, 0.2 mm i.d., fused silica capillary column, SUPELCOWAX 10. The GC response peaks were integrated with a Hewlett-Packard 3396 integrator. Column, injector, and detector temperatures were (423, 473, and 523) K for all the measurements. Very good separation of peaks was achieved under these conditions, and calibration analyses were carried out to convert the peak area ratios to the mass composition of the sample. At least three analyses were made of each extract composition; the standard deviation in the mole fraction was usually less than ±0.001.

Results and Discussion

The solubilities of the ternary system limonene + linalool in supercritical carbon dioxide were determined at 318.2 K and 328.2 K. Pressures ranged from (70 to 110) bar, while two different mixtures of limonene + linalool were used in order to obtain information about the influence of the initial composition. A 40 mass % limonene + 60 mass % linalool mixture and a 60 mass % limonene + 40 mass % linalool mixture were the values selected. The obtained values of these solubilities are shown in Table 2 and Figure 1.

Table 1. Critical Constants and Acentric Factors of Components

substance	T_c/K	P_c/bar	ω
CO_2	304.2[a]	73.7[a]	0.225[a]
limonene	660.0[a]	27.5[a]	0.312[a]
linalool	630.5[b]	24.2[b]	0.748[c]

[a] Daubert and Danner.[27] [b] Estimated by the Lydersen method.[28] [c] Estimated by the Edmister method.[28]

Table 2. Solubilities of Limonene (y_1) and Linalool (y_2) in Supercritical CO_2

	40 mass % limonene + 60% mass linalool mixture		60 mass % limonene + 40 mass % linalool mixture			
	45 °C		45 °C		55 °C	
P/bar	y_1	y_2	y_1	y_2	y_1	y_2
70	0.0040	0.0031	0.0036	0.0010	0.0080	0.0040
74	0.0064	0.0069	0.0042	0.0015	0.0082	0.0040
78	0.0076	0.0098	0.0048	0.0019	0.0083	0.0041
82	0.0128	0.0167	0.0101	0.0067	0.0089	0.0046
86	0.0242	0.0339	0.0242	0.0152	0.0100	0.0053
90	0.0536	0.0760	0.0655	0.0407	0.0130	0.0062
95					0.0207	0.0074
100					0.0306	0.0152
105					0.0458	0.0252
110					0.0975	0.0436

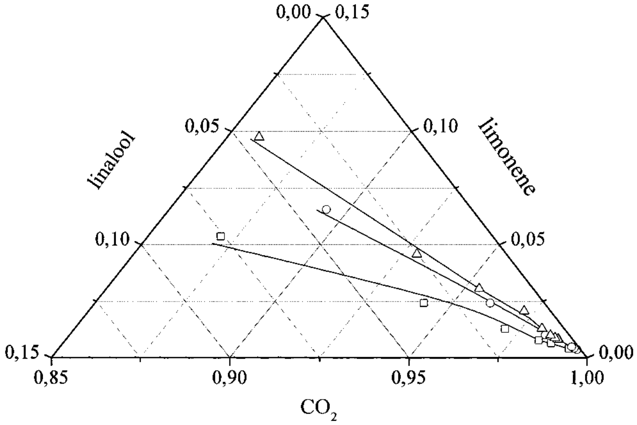

Figure 1. Solubility data (y/mole fraction) of the system limonene (1) + linalool (2) + CO_2 (3). 40 mass % limonene + 60 mass % linalool: (□) 318.2 K. 60 mass % limonene + 40 mass % linalool: (○) 318.2 K and (△) 328.2 K. (−) PR EOS modeling.

At a constant temperature, raising the pressure increases the density of the supercritical fluid; that is, its solvating power becomes greater and more solute is transferred from the liquid to the vapor phase. On the other hand, at a constant pressure, under 80 bar, one observes that raising the temperature increases the solubility of limonene or linalool. In this case, the reduction in solvent density, that is, the decrease in its solubilization capacity due to an increase in temperature, is overcome by the effect of increasing the solute vapor pressure. At pressures over 80 bar, the solubility of both compounds decreases with increasing temperature; in other words, the more important effect is the decrease of the solvent density. This behavior was found in the binary systems.[12] Finally, increasing the amount of solute fed to the system increases the solute solubility.

The comparison between our results and those of other authors[3,20,23] for the ternary system shows a similar behavior versus temperature and pressure. The comparison between our experimental and literature data was shown in Figure 2. There are discrepancies among the literature data of the corresponding binary systems.[12] These discrepancies were also found in the ternary system, as shown in Figure 2.

Figure 3 shows the selectivity data for the system, defined as $y_{limonene}/y_{linalool}$. At a constant temperature, raising the pressure decreases the selectivity because of

Table 3. Calculated Parameters and Deviations between Experimental and Calculated Values for Different Models for the System Limonene (1) + Linalool (2) + CO_2 (3)

	T = 318.2 K							T = 328.2 K						
model	κ_{12}	κ_{13}	κ_{23}	η_{12}	η_{13}	η_{23}	ARD	κ_{12}	κ_{13}	κ_{23}	η_{12}	η_{13}	η_{23}	ARD
Peng−Robinson	0.015	0.111[a]	0.052[a]	−0.018	−0.010[a]	−0.035[a]	0.033	0.053	0.111[a]	0.052[a]	−0.056	−0.010[a]	−0.035[a]	0.025
Soave−Redlich−Kwong	0.014	0.199	0.044	−0.177	−0.135	−0.198	0.036	0.053	0.089	0.060	−0.055	−0.017	−0.037	0.021

[a] Generalized binary interaction parameters from Berna et al.[12] ARD = $1/N\sum|y_{cal} - y_{exp}|/y_{exp}$.

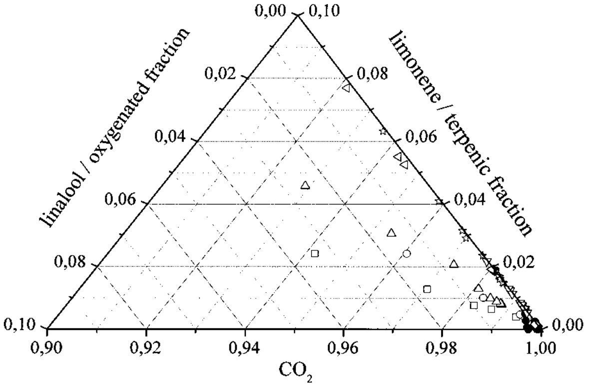

Figure 2. Comparison between data of this work and literature data of the systems limonene (1) + linalool (2) + CO_2 (3) and orange peel oil + CO_2. This work: 40 mass % limonene + 60 mass % linalool, (□) 318.2 K; 60 mass % limonene + 40 mass % linalool, (○) 318.2 K and (△) 328.2 K. Literature data for the system limonene (1) + linalool (2) + CO_2 (3): (◇) 323.2 K;[20] (▲) 313.2 K, (●) 333 K.[23] Solubility of the system orange peel oil + CO_2:[29] (▼) 323.2 K; (☆) 333.2 K; (left open triangle) 343.2 K.

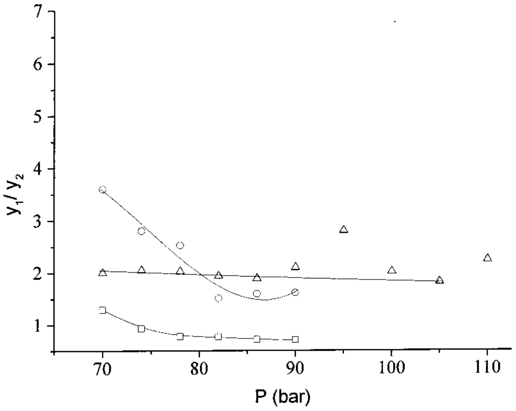

Figure 3. Selectivity data (y_1/y_2) for the system limonene (1) + linalool (2) + CO_2 (3). 40 mass % limonene + 60 mass % linalool: (□) 318.2 K. 60 mass % limonene + 40 mass % linalool: (○) 318.2 K and (△) 328.2 K splint line.

an increase in the solvating capacity of the supercritical solvent (effect of higher density of the solvent). On the other hand, at a lower pressure (79−95) bar, raising the temperature causes the selectivity to decrease quickly because of a decrease in the density of the solvent. Finally, increasing the limonene amount fed causes the selectivity to rise. In summary, the selectivity varies for the limonene and linalool because of the variation of solvent density, due, their molecular weights and vapor pressures being similar, mainly to the linalool polar nature.

Our data are indicative of a possible selective deterpenation of orange peel oil, with the selectivity being ~2 in approximating the real composition of the oil (limonene ≅ 90−95%). This conclusion is in agreement with the conclusions of other authors.[3,20,23] For instance, the value of the selectivity between limonene and linalool at 328.2 K and 110 bar is 2.24 (Figure 2), which is less than that calculated from the binary solubility data (8.5 at the same conditions).[12] This is evidence that molecular interactions between limonene and linalool cannot be neglected. It also suggests that relevant errors can be made when only binary VLE behavior analysis is included in the designing of a supercritical extraction process.

Table 4. Generalized Calculated Parameters and Deviations between Experimental and Calculated Values for Different Models for the System Limonene (1) + Linalool (2) + CO_2 (3)

model	κ_{12}	κ_{13}	κ_{23}	η_{12}	η_{13}	η_{23}	ARD[a]
Peng−Robinson	0.158	0.021	0.024	−0.099	−0.025	−0.017	0.175
Soave−Redlich−Kwong	0.011	0.091	0.054	−0.109	−0.025	−0.017	0.365

[a] ARD = $1/N\sum|y_{cal} - y_{exp}|/y_{exp}$.

This behavior shows that the best conditions for supercritical extraction must be optimized between high selectivity and high solubility, to obtain the maximum amount of product with the best quality, in other words, a higher proportion of oxygenated compounds.[3,20,23]

The solubilities are successfully correlated using equations of state (EOS's), as shown in Figure 1. The parameters used and the average relative deviation (ARD) are shown in Tables 3 and 4.

The parameters was determined at each temperature by minimizing the following objective function:

$$\mathrm{OF} = \sum\left(\frac{\mathrm{ABS}(y_{exp} - y_{calc})}{y_{exp}}\right) \qquad (1)$$

where y is the mole fraction of solute (linalool or limonene) in the supercritical phase.

The results of the ternary system modeled using only the parameters fixed from binary data, limonene + CO_2, linalool + CO_2,[12] and taking the parameters for limonene + linalool to be zero were very poor (ARD = 0.690). So, the marked variation of the selectivity calculated from the binary systems and its values calculated from the ternary data at the same conditions of temperature and pressure must be taken into account in the determination of the interaction parameters between limonene and linalool.

The values for κ_{13}, κ_{23}, η_{13}, and η_{23} for the PR EOS were obtained in a previous work[12] using the binary data. The values for κ_{12} and η_{12} for the PR EOS in Table 3 were determined by using the ternary data. However, although the deviation is smaller for the SRK EOS in this table (calculated only with the ternary data), it must be noticed that the determination of PR EOS parameters has been made using a higher number of experimental data (46), in other words, both ternary and binary figures.

Table 4 gives the parameters for both EOS's obtained using all ternary data. It is an attempt to find parameters that can predict the ternary data for all conditions of temperature and pressure. Although the deviation is larger in both cases, the results for the PR EOS show that they can predict with more acceptable deviation the vapor composition.

In conclusion, the present work has been undertaken to explain two important points of phase behavior for the system limonene + linalool + CO_2: first of all, to study the possibility of a selective separation of the terpenic (limonene) and oxygenated (linalool) fractions from orange peel oil using supercritical CO_2, and second of all, to obtain the solubility data for modeling and simulating the oil deterpenation process in a supercritical fluid extraction column.

Experimental results show that not only should binary solubility data be considered in modeling multicomponent systems at high pressures but also ternary solubility data are necessary for modeling. For instance, values for the selectivity between limonene and linalool from the ternary solubility data are lower than those obtained from the binary solubility data. This fact suggests that molecular interaction between limonene and linalool cannot be neglected because accurate thermodynamic modeling of this kind of behavior is crucial in a developing separation process.

The selectivity values obtained indicate that an efective separation of limonene and linalool can be achieved.

In using supercritical CO_2 as an extractive agent for citrus oil, the conditions for the desirable yields of oxygenated flavor compounds must be optimized between high selectivity and high solubility.

The present data are well correlated by the PR EOS and the SRK EOS. The best results have been obtained using interaction parameters between limonene and linalool. Finally, generalized EOS parameters were found for the ternary system limonene + linalool + CO_2. These parameters allow a reasonable prediction of the ternary vapor phase for any pressure or temperature. For the ternary system, the PR EOS has given the best fit.

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Received for review January 22, 2001. Accepted May 16, 2001. The authors acknowledge CICYT for their financial support (Project 1FD97-1246-CO3).

JE010029Y