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Solubilities of Essential Oil Components of Orange in Supercritical Carbon Dioxide

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The solubilities of pure limonene and linalool in compressed carbon dioxide have been measured using a flow apparatus at 318.2 K and 328.2 K and pressures ranging from 69 bar to 111 bar. The solubilities were successfully modeled using equations of state (Peng−Robinson, Soave−Redlich−Kwong, 3P1T, Dohrn and Prausnitz nopolar) and a semiempirical equation (Chrastill model). The generalized parameters for the Peng−Robinson EOS were obtained for each system. These parameters were independent of temperature, and they reproduce successfully all data available in the literature. The results show that the solubility of limonene in supercritical carbon dioxide was bigger than the solubility of linalool. The behavior of the systems was discussed by estimation of the best conditions of supercritical extraction. Those conditions were elevated pressure and a temperature near the critical temperature of carbon dioxide.

Introduction

Supercritical fluids have been proposed for important application in the field of extraction, analysis, materials, and reactions (Mc Hugh and Krukonis;[1] Stahl and Gerard[2]). On the other hand, citrus essential oils are widely used as a raw material of flavor in food and perfumery industries. They are conventionally processed by distillation or solvent extraction, resulting in the thermal degradation of some valuable compounds.

The high-pressure vapor−liquid equilibria for CO_2 + citrus oil are required for rational equipment design, and some measurements on the system are available (Sato et al.;[3] Reverchon[4]). A common practice to study each citrus oil is to consider it as a binary synthetic mixture of its two more important components (Mira et al.;[5] Kalra et al.;[6] Sato et al.[7]). For instance, the cold-pressed orange oil is usually treated as a mixture of limonene and linalool, representing the terpene and the oxygenated fractions, respectively.

Some binary phase equilibria and solubility data of limonene and linalool in supercritical CO_2 can be found in the current literature (Iwai et al.;[8,9] Matos et al.;[10] Di Giacomo et al.[11]). It can be noticed that there is more information about the system limonene + CO_2. These papers studied this system at 323.15 K, and they show some disagreements among these data. Also, the studied intervals of the pressures are nonhomogeneous; this fact makes difficult the global treatment of this information. On the other hand, only Iwai et al.[8,9] have modeled their data at the different temperatures, but they have used only the Peng−Robinson EOS (Peng and Robinson[12]). On the other hand, in supercritical systems, parameters obtained for a fixed temperature used in the estimation of the solubility at another temperature normally provide poor results.

In this work, the bases for a proper answer to the selectivity problem between the two cited compounds are reported. The objective of this work is to measure the solubilities of the systems linalool + CO_2 and limonene + CO_2, to have a complete experimental base to study the capacities of the different models for the correlation of these data. So, we will have comparable information to interpret the behavior of the ternary system. Like this, the experimental procedure and behavior of these systems was validated. The results obtained were correlated by some equations of state (Peng−Robinson EOS (Peng and Robinson[12]); Soave−Redlich−Kwong EOS (Soave[13]); 3P1T (Yu and Lu[14]); and Dohrn−Prausnitz nopolar (Dohrn and Prausnitz[15])) and a semiempirical equation (Chrastill[16]). Finally, generalized parameters of the systems limonene + CO_2 and linalool + CO_2 were successfully obtained. These parameters were useful for any temperature in the work interval.

Models. The following equations of state were used: Peng−Robinson (Peng and Robinson[12]), eq 1; Soave−Redlich−Kwong (Soave[13]), eq 2; 3P1T (Yu and Lu[14]), eq 3; and Dohrn−Prausnitz nopolar (Dohrn and Prausnitz[15]), eqs 4−6; while the semiempirical model was by Chrastill (Chrastill[16]), eq 7.

$$P = \frac{RT}{\nu - b} - \frac{a(T)}{\nu^2 + 2b\nu - b^2} \tag{1}$$

$$P = \frac{RT}{\nu - b} - \frac{a(T)}{\nu(\nu + b)} \tag{2}$$

$$P = \frac{RT}{\nu - b} - \frac{a}{\nu(\nu + d) + b(3\nu + d)} \tag{3}$$

$$Z = Z_{\text{ref}} + Z_{\text{pen}} \tag{4}$$

$$Z_{\text{ref}} = \frac{1 + \left(\frac{3DE}{F} - 2\right)\eta + \left(\frac{3E^3}{F^2} - \frac{3DE}{F} + 1\right)\eta^2 - \frac{E^3}{F^2}\eta^3}{(1 - \eta)^3} \tag{5}$$

$$D = \sum_{i=1}^{N} \xi_i \sigma_i \tag{6}$$

$$c = \rho^{\kappa} \exp\left(\frac{a}{T} + b\right) \tag{7}$$

In eqs 1−7, ν is the molar volume; P is the pressure; T is

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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	662.6[b]	27.5[b]	0.310[c]
linalool	630.5[b]	24.2[b]	0.748[c]

[a] Daubert and Danner.[18] [b] Estimated by the Lydersen method (Reid et al.[19]). [c] Estimated by the Edmister method (Reid et al.[19]).

the temperature; R is the universal gas constant; a, b, d, and κ are parameters of the equations; ξ is the mole fraction; ρ is the molar density; c is the molar concentration; η, D, E, F, Z_{pen}, and σ are functions of the parameters of the equations; and the subscripts i and j correspond to different components.

The critical properties and acentric factors of the pure components used in this work are listed in Table 1, and the following conventional mixing rules have been considered:

$$a_{ij} = \sqrt{a_i a_j}(1 - k_{ij}) \tag{8}$$

$$a_{ij} = \frac{b_i + b_j}{2}(1 - \eta_{ij}) \tag{9}$$

where a_i, a_j, b_i, and b_j are the parameters of pure components and k_{ij} and η_{ij} are binary adjustable interaction parameters. Other mixing rules were tried without improving results.

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

Equipment and Procedure. Solubilities were measured with an SFX 3560 extractor with two model 260D syringe pumps manufactured by ISCO (Lincoln, NE). With the proper plumbing, the two-pump system can deliver a continuos flow of supercritical fluid. A modifier can be added. The cylinder capacity of the pump is 266 mL and the maximum pressure 510 atm. The temperature can range from 313.2 K to 423.2 K, and the 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 (limonene or linalool) was added to the diatomaceous earth in the cartridge. The role of this material is to avoid the draining of the liquid.

Table 2. Solubilities (y) of Linalool (3) and Limonene (2) in CO_2 (1)

linalool (3) + CO_2 (1)				limonene (2) + CO_2 (1)	
T = 318.2 K		T = 328.2 K		T = 318.2 K	
P/bar	10^3y/mole fraction	P/bar	10^3y/mole fraction	P/bar	10^3y/mole fraction
71	0.680	71	0.69	69	1.70
77	1.05	79	0.80	76	2.41
84	2.53	85	1.39	81	3.94
91	17.40	91	1.99	85	9.53
96	282.60	96	3.39	90	22.92
		100	30.39	95	108.31
		106	104.21	100	173.23
		111	212.72	105	279.70

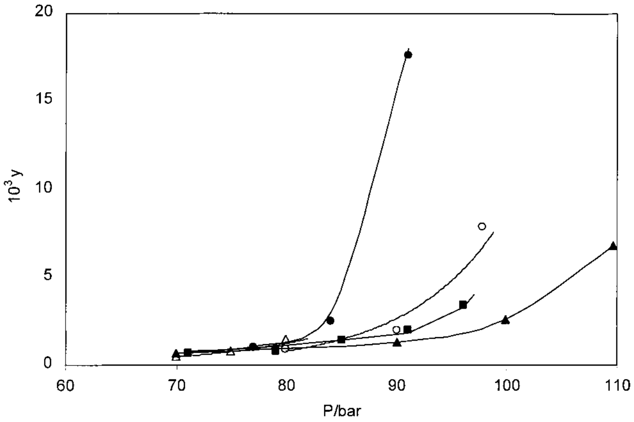

Figure 1. Solubilities of the system linalool (3) + CO_2 (1). Values from this work: ●, at 318.15 K; ■, at 328.15 K. Values from Iwai et al.:[8] △, at 313.15 K; ○, at 323.15 K; ▲, at 333.15 K. (−) Peng−Robinson EOS (Peng and Robinson[12]) with generalized parameters.

The extract was analyzed by supercritical chromatography. A Suprex (Pittsburgh, PA) MPS/225 supercritical chromatograph with a syringe pump was used. The syringe pump allows a maximum pressure of 500 atm, and its capacity is 250 mL. This pump provides a pulse-free mobile stream at low flow rates, an interesting advantage when used with a flame ionization detector (FID). The sample solution was injected into a flow of supercritical CO_2 via a four-port valve with a 1 μL internal volume loop.

A stainless steel column (25 cm × 4.6 mm i.d.), Nucleosil C-18 (5 μm) (Keystone Scientific, Bellefonte, PA), was used in the SFC determination. One of the ports of the injection valve was connected to the column, and this was introduced into the oven. A fused silica tube, used as a restrictor, was connected from the end of the column to the FID. It provided back-pressure, which is necessary to maintain supercritical conditions in the system.

Results and Discussion

The solubilities of linalool in supercritical carbon dioxide were determined at 318.2 K and 328.2 K, while the solubilities of limonene were determined only at 318.2 K. Pressures ranged from 69 to 111 bar. The obtained values of these solubilities are shown in Table 2 and Figures 1 and 2 together with literature data. They were measured in order to complete the literature. The system limonene + CO_2 was not studied more widely because limonene appears in a lot of essential oils and there is extensive literature about it.

From these values it can be seen that the solubility of limonene in supercritical carbon dioxide is bigger than the solubility of linalool at the same conditions but that at

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

	linalool (3) + CO_2 (1)						limonene (2) + CO_2 (1)		
	T = 318.2 K			T = 328.2 K			T = 318.2 K		
model	κ_{12}	η_{21}	ARD	κ_{12}	η_{21}	ARD	κ_{12}	η_{21}	ARD
Peng−Robinson[a]	0.072	−0.092	0.0242	0.061	−0.039	0.0024	0.119	−0.032	0.0187
Soave−Redlich−Kwong[a]	0.077	−0.082	0.0281	0.070	−0.106	0.0028	0.124	−0.039	0.0186
3P1T[a]	0.073	−0.066	0.0282	0.067	−0.070	0.0023	0.114	−0.028	0.0209
Dohrn−Prausnitz nopolar[a]							0.058	0.095	0.0271
Chrastill[b]	k = 4.47	a = 100 040.33		b = −52.43	ARD = 0.0016				

[a] EOS. [b] Semiempirical equation (both temperatures). ARD = $1/N\sum(|y_{\rm cal} - y_{\rm exp}|/y_{\rm exp})$.

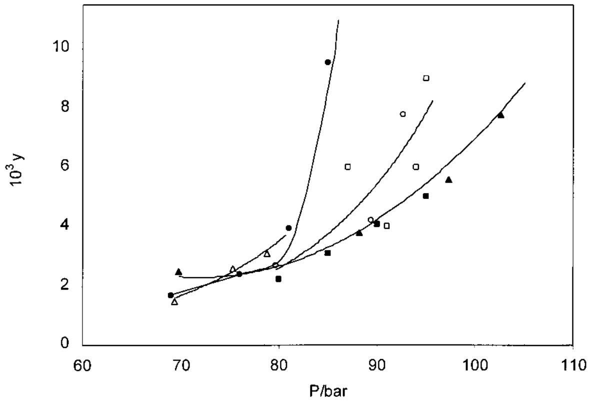

Figure 2. Solubilities of the system limonene (2) + CO_2 (1). Values from this work: ●, at 318.15 K. Values from Iwai et al.:[9] △, at 313.15 K; ○, at 323.15 K; ▲, at 333.15 K. Values from Matos et al.:[10] □, at 323.15 K. Values from Di Giacomo et al.:[11] ■, at 323.15 K. (—) Peng−Robinson EOS (Peng and Robinson[12]) with generalized parameters.

bigger pressures they approach each other. Also, both systems show a sudden increase in the solubility at pressures up to approximately 80 bar.

In the linalool−CO_2 system, it can be noticed that when the temperature rises at pressures under 80 bar, the solubility increases but that, at pressures over 80 bar, the solubility decreases. This behavior shows that the critical pressure of the mixture is probably near 80 bar.

The comparison between our results and those of other authors for the system limonene + CO_2 shows that the solubility increases when the temperature rises at pressures under 80 bar but that, at pressures over 80 bar, it decreases. So, the critical pressure of the system is near this value. It can be observed that this behavior is similar to that of the system linalool + CO_2.

This behavior shows that the best conditions for supercritical extractions in both systems will be a pressure > 90−100 bar and a temperature near the critical temperature of carbon dioxide in order to obtain the maximum amount of product. Our results are in agreement with those of kinetic studies which fixed the best pressure for the extraction or deterpenation of citrus oil peel at about 200 bar (Reverchon;[4] Mira et al.[5]). A bigger pressure carries operational problems and costs too elevated.

The solubilities are widely and successfully modeled using equations of state and semiempirical equations. The parameters of the equations of state were determined using the PE program (Pfohl et al.[17]). These parameters and the average relative deviation (ARD) are shown in Table 3, and they are similar to those available in the literature for the Peng−Robinson EOS (Peng and Robinson[12]) (Iwai et al.[8,9]).

The semiempirical model of Chrastill (Chrastill[16]) shows better results in the correlation of experimental values.

Table 4. Generalized Parameters and Deviations between Experimental and Calculated Values for the Peng−Robinson EOS

system	κ_{12}	η_{21}	ARD[a]
linalool (3) + CO_2 (1)	0.052	−0.035	0.0364
limonene (2) + CO_2 (1)	0.111	−0.010	0.0454

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

The parameter estimation was performed at each temperature by minimizing the following objective function:

$$\mathrm{OF} = \sqrt{\frac{1}{N}\sum\left(\frac{y_{\rm cal} - y_{\rm exp}}{y_{\rm exp}}\right)^2} \tag{10}$$

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

The Peng−Robinson EOS generalized parameters (Peng and Robinson[12]) were obtained for each system, linalool + CO_2 and limonene + CO_2, using the literature information, our experimental data, and the PE program (Pfohl et al.[17]) and taking the parameters as independent of temperature. These parameters are shown in Table 4. Other EOSs, such as Soave−Redlich−Kwong (Soave[13]) and 3P1T (Yu and Lu[14]), were tried without improving results. The PR EOS was chosen because it is more frequently used in the systems studied. The generalized parameters of the PR EOS reproduce successfully all data available in the literature for the supercritical region. This is very important for design of future plants and to predict these systems at any conditions of pressure and temperature. Figures 1 and 2 show that the behavior of the solubilities and the generalized parameters obtained in this work was widely applicable to data in the literature. So, these conclusions can be generalized for the binary systems.

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