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Supercritical Equilibrium Data of the Systems Carbon Dioxide—Linalool and Carbon Dioxide—Orange Essential Oil

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ABSTRACT

In this paper experimental equilibrium data on the system supercritical CO_2-orange essential oil and the system supercritical CO_2-linalool are reported at 323.15 K and 343.15 K, for pressures in the ranges of 7.6 - 13.5 MPa. The behavior of the system supercritical CO_2-orange essential oil was represented by means of thermodynamic model, based on Peng-Robinson equation of state. To this aim the orange essential oil was represented by a mixture of limonene, linalool and β-caryophyllene, selected to represent the classes of monoterpenes, oxygenated terpenes and sesquiterpenes respectively. The model uses only regression parameters calculated from binary sub-systems, CO_2-limonene and CO_2-β-caryophyllene (taken from literature) and CO_2-linalool (calculated from the fitting of original data reported in the present work) thus being predictive with respect to the multicomponent mixture.

Keywords: Supercritical; Extraction; Carbon Dioxide; Orange Essential Oil; Linalool; Phase Equilibrium

1. Introduction

The so called citrus essential oils are by means of a mechanical extraction process: they are extensively used in the food (beverage, sweets etc.), cosmetics and pharmaceutical industry, mainly because of its fragrance and flavor.

These natural matrices are very complex and contain an extremely large number of components (more than one hundred), and, in the classical approach, components are lumped in classes of homogeneous physical and chemical characteristics. Each class is then represented by a single component (the component showing the higher concentration is the one usually chosen). In the field of citrus essential oils three classes of more or less volatile components are usually considered: the monoterpenes, unsaturated hydrocarbon with 10 carbon atoms, the oxygenated terpenes which show the same number of carbon atoms but contain an oxygenated group (alcoholic, aldheidic, esteric or ketonic) and the sesquiterpenes, molecules with a higher number (15) of carbon atoms [1].

Citrus essential oils are characterized by different concentrations of the three classes of compounds; in particular lemon essential oil has a content of terpenes lower (approximately 94%) than the ones contained in orange essential oil (98% - 99%). On the contrary the monoterpene concentration in bergamot essential oil is very different (equal to about 50%) [2,3]. The fragrance of the oil mainly depends on the type and concentration of oxygenated components present in it, while the terpenes provide a very poor contribution. The deterpenation process consists in the selective extraction of terpenes from natural matrix, thus producing a more valuable raffinate enriched in oxygenated compounds [4-6]. This process can be carried out through a thermal process (mainly vacuum distillation) or by supercritical extraction with CO_2 as solvent. In fact supercritical CO_2 has a solvent power on monoterpene compounds higher than the power it has on the oxygenated ones, so an extract enriched in monoterpenes and a raffinate enriched in oxygenates can be obtained.

The extraction process may be continuous or discontinuous and can be carried out in different apparatus (a simple extraction vessel or a countercurrent column with enrichment and exhaustion sections, with internal or external reflux). The modelization and optimization of the

extraction equipment require the knowledge of the equilibrium data of the system CO_2-natural complex mixture (for example orange essential oil), as a function of operational temperature and pressure. Such experimental data are generally poor, except in the case of lemon essential oil, which has been studied most extensively [7-10]. Anyway the available experimental data generally refer to solubility data e.g. data on solubility of CO_2 in the oil and solubility of oil in supercritical CO_2. In some works the CO_2-citrus essential oil system is assimilated to a pseudo binary system and no information is given about the equilibrium concentrations of main classes of components (monoterpenes, oxygenated terpenes and sesquiterpenes) in supercritical and liquid phases.

Just a few orange essential oil experimental data are actually available, furthermore, the oil is assimilated to a two pseudocomponents [11,12], monoterpenes and "aroma" components. The aim of this paper is to present experimental equilibrium data of the system CO_2-orange essential oil. In particular, in the range of temperature and pressure widely used in deterpenation process (*i.e.* temperatures ranging from 323.15 K to 343.15 K and pressures from 7 to 13 MPa), solubility data and equilibrium concentration data of CO_2 and different classes (monoterpenes, oxygenated terpenes and sesquiterpenes), in supercritical and liquid phases will be presented. This approach is similar to the one followed recently to study the system CO_2-Lemon essential oil [10].

Furthermore, the thermodynamic modelization of the system CO_2-orange essential oil will be presented by means of Peng Robinson equation of state (PREOS). As pointed out above, the complex mixture is assimilated to a simple mixture of the components that are assumed to represent each class. For example in the previous papers dealing with lemon essential oil [5,6,10], limonene, citral e β-caryophyllene have been assumed to represent monoterpene, oxygenated terpenes and sesquiterpene classes. In the modelization only binary interaction parameters between CO_2 and each component in the mixture representing the oil are used to increase the reliability of the method. These parameters are obtained from regression of binary equilibrium data of the systems CO_2-limonene, CO_2-Citral, CO_2-β-caryophyllene in the temperature range of interest, and its values are reported in literature. Dealing with orange essential oil, the same compounds can be selected to represent monoterpene and sequiterpene classes, but for oxygenate class another compound, linalool, is more suitable for the modelization of the whole class, instead of cytral.

Unfortunately scarce experimental data about the system CO_2-linalool are available, so equilibrium data about this system at temperature of 323.15 K and 343.15 K and pressure ranging from 7.6 to 13.2 MPa have been measured in this work. Optimal values of binary interaction parameters for the system CO_2-linalool have been determined by the fitting of experimental data by means of PR EOS.

Once all the binary interaction parameters are available and after having defined the concentration of various components in the oil, the model can be applied to the modelization of the CO_2-orange essential oil system. The method is purely predictive because no other regression parameter has been used to represent equilibrium data of the multicomponent system CO_2-orange essential oil.

A comparison between predicted and experimental values of equilibrium data of the system CO_2-orange essential oil shows that the model is able to represent both solubility data and equilibrium compositions of liquid and supercritical phases at 323.15 K and 343.15 K. In particular this model correctly evaluates equilibrium ratios of the four components in the mixture (CO_2, limonene, linalool and β- caryophyllene) at different operational pressure and temperature: therefore, the model can be used in a process simulator to design and to optimize the deterpenation equipment.

2. Materials and Methods

2.1. Materials

The essential oil used in this work was purchased from Simone Gatto (Sicily, Italy), and was obtained by cold-pressing orange peels. The oil was stored at 248 K and filtered before use in order to remove waxes. The composition of the oil was determined by means of Gas Chromatographic (GC) analysis, according to the procedure reported in detail elsewhere [5]. All components reported in the GC analysis of orange oil were grouped in terms of the three main classes of compounds: monoterpenes (mt), oxygenated terpenes (ox), and sesquiterpenes (st).

The mean composition of the feed oil, obtained from five GC analyses, resulted to be (mass percent, average value and standard deviation): mt 99.05% ± 0.25%, ox 0.82% ± 0.21% and st 0.13% ± 0.05%. The same procedure, repeated five times, was also applied in the measurements of the composition of supercritical and liquid phases in the equilibrium experiments.

CO_2 used in this work is 99.9% pure (Siad, Italy). Linalool (dimethyl-1,6-octadien-3-ol) 97% pure was purchased from Sigma-Aldrich (FW 154.25) and was used without further purification

Ethanol p.a. 99.8% (Fluka Chemical), was utilized to dilute (1:10) the samples of oil before the GC analysis.

2.2. Experimental Methods

The apparatus used in the present work was developed and utilized in previous works [13-15] dealing with high-pressure phase equilibrium measurements of binary

systems composed of CO_2 and relevant compounds of lemon essential oil and measurements of the pseudo binary system CO_2-lemon essential oil [10]. In particular work [13] reports a detailed description of both the apparatus and the experimental methodology.

The experimental plant is composed of two cylindrical chambers of 170 cm^3 each (i.d. 16 mm), equipped with heating jackets for temperature control. One of the two chambers (the equilibrium chamber) is initially loaded with about 30 grams of liquid (linalool or orange essential oil) whereas the other (gas chamber) is initially empty. At the beginning of the run CO_2 is fed to both chambers up to the desired pressure. The apparatus is equipped with a recirculation pump that extracts the gaseous phase from the bottom of the gas chamber and re-injected it at the bottom of the equilibrium chamber to increase mass transfer between supercritical and liquid phases.

According to our experience on this apparatus, a recirculation time equal to almost 6 hours and a flow rate of recirculating supercritical phase equal to about 500 Nliters/min have to be utilized to be sure to attain equilibrium conditions.

After the recirculation period, the two chambers are separated by closing valves in order to allow the whole content of the gas chamber to be sampled without disturbing the equilibrium conditions in the equilibrium chamber. The sampling of gas and liquid phases is carried out according to the procedure described in detail elsewhere [14]. The amount of solute collected during gas and liquid sampling was determined gravimetrically, whereas the amount of CO_2 is determined by means of the gas meter connected to the experimental apparatus (accuracy equal to 0.001 Nliters).

The amount of liquid collected from the gas phase sampling (pure linalool or orange essential oil extract) resulted to be in the range of 0.13 - 12.3 g, with a sampled volume of CO_2 in the range of 19.5 - 56 l (measured at ambient conditions). As far as the liquid phase sampling is concerned, the amount of liquid withdrawn from the bottom of the equilibrium chamber resulted to be in the range of 0.23 - 1.46 g.

A small amount of liquid oil collected from gas and liquid phase sampling were analyzed chromatographically in order to determine their composition, on CO_2 free basis.

At the end of each experimental run the equilibrium chamber is depressurized and mass of oil was determined gravimetrically in order to check the oil mass balances referred to the whole experimental run. On the contrary no check can be done by means of CO_2 mass balance because it is not known the mass of CO_2 initially fed to the apparatus. Anyway the volume of CO_2 exiting the chamber in the depressurization step is measured and both added to the volume of CO_2 measured during the extraction of the gaseous phase from the gas chamber and to the volume developed during the sampling of the liquid phase. This way, in the hypothesis that no loss of CO_2 occurred during the experiment, the total amount of CO_2 fed to the apparatus is evaluated. So it is possible to evaluate the initial overall composition of the system.

3. Experimental Results

3.1. Carbon Dioxide—Linalool

The phase equilibrium data for the binary system CO_2-linalool are measured at 323.15 K and 343.15 K, in the pressure ranges 8.3 - 10.5 MPa and 10.1 - 13.5 MPa, respectively, with the experimental set-up and with the procedure described in the previous Section 2.

Table 1 reports the solubility of linalool in supercritical CO_2 phase (linalool solubility, sg) and the solubility of CO_2 in liquid linalool (CO_2 solubility, sl), at the indicated temperatures.

Figure 1 shows the experimental points and the model curves for the linalool solubility, as a function of the pressure, at the temperatures of 323.15 K and 343.15 K. These values are compared with the data from literature at 313.15, 318.15, 323.15, 328.15 and 333.15 K [16,17]. Linalool solubility is expressed as grams of linalool per kilogram of CO_2. The solubility of linalool measured in this work, increases with the pressure, at fixed tempera-

Table 1. Experimental solubility of linalool in supercritical CO_2 (sg) and solubility of CO_2 in the liquid linalool (sl) at 323.15 K and 343.15 K as function of pressure.

T (K)	linalool - carbon dioxide		
	P (MPa)	sg (g/1000 g)	sl (g/g)
323.15	8.250	9.815	0.590
	8.600	11.856	0.745
	8.650	16.589	0.856
	9.200	16.927	1.296
	9.840	28.429	2.055
	10.083	47.985	3.775
	10.464	123.540	5.200
343.15	10.100	16.610	0.571
	10.900	20.007	0.749
	11.500	26.380	0.797
	11.900	36.215	0.877
	12.300	43.015	1.107
	12.700	50.171	1.274
	13.000	56.699	1.546
	13.100	68.163	1.570
	13.500	96.704	2.139

ture, in the range of 9.8 - 123.5 g/kg at 323.15 K, and in range of 16.6 - 96.7 g/kg at 343.15 K. The trends of literature data, at the five different temperatures, are consisted with the behavior of the experimental data and with the model curves presented in this work.

Figure 2 compares the experimental data reported in this work and the model curves of the CO_2 solubility, as a function of the pressure, at the temperatures of 323.15 and 343.15 K with data from literature at 313.15, 323.15 and 333.15 K [17]. The solubility in liquid phase is expressed as grams of CO_2 per gram of linalool. The solubility of CO_2 measured in this work, increases with the pressure in the ranges of 0.59 - 5.2 g/g at 323.15 K, and in ranges of 0.57 - 2.14 g/g at 343.15 K and decreases with the temperature in the considered pressure ranges. These trends are in agreement with the literature data

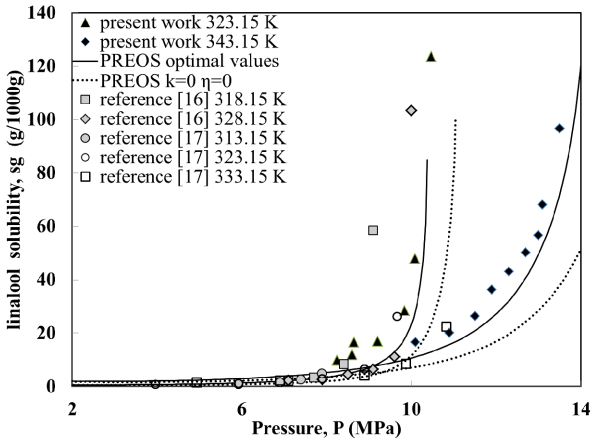

Figure 1. Experimental data presented in this work, literature data and model curve for solubility of linalool in supercritical CO_2 at 323.15 K and 343.15 K as function of pressure.

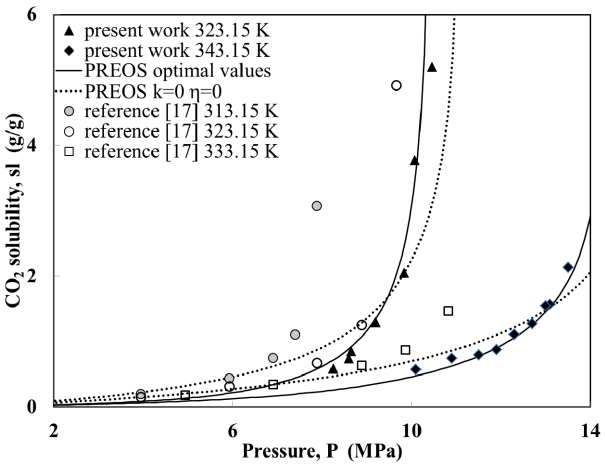

Figure 2. Experimental data presented in this work, literature data and model curve for solubility of CO_2 in the liquid linalool at 323.15 K and 343.15 K as function of pressure.

even if the values reported in reference [17] are higher than the values of solubility measured in this work at 323.15 K, after 8.9 MPa. However, it has to be underlined that in this region solubility increases greatly.

3.2. Carbon Dioxide—Orange Oil

The gas-liquid phase equilibrium of the system CO_2-orange essential oil was investigated at 323.15 K and 343.15 K, for pressures in the ranges of 7.6 - 9.6 MPa and 10.1 - 13.2 MPa, respectively. The maximum value of pressure used is the value in correspondence of which, at each temperature, there are two phases in equilibrium conditions. The chosen range of pressure and temperature values are particularly relevant for this system, since they represent potential operating parameters for the efficient application of the supercritical deterpenation process. The experimental data on the system CO_2-orange essential oil are collected in **Table 2** and their trends are shown in **Figures 3** and **4**.

Figure 3 shows the solubility of the oil in supercritical CO_2 (sg) as a function of pressure, at the two temperatures under investigation. The data measured in this work show that at 323.15 K the solubility of the oil increases from approximately 11 to 21 g/kg, for pressures ranging from 7.6 MPa to 9.6 MPa; at 343.15 K the solubility increases from approximately 16 to 75 g/kg, for pressures ranging from 10 MPa to 13 MPa. In the same **Figure 3** a comparison with literature experimental data [12] is also reported. Actually in **Figure 3** it was not possible to represent the experimental data of solubility of orange essential oil in CO_2 [12] as in the original work these data are reported only in a figure. On the other hand in the same work is given an empirical correlation of experimental solubility data that perfectly represents the experimental data themselves. Therefore, to test the relia-

Table 2. Experimental solubility of orange oil in supercritical CO_2 (sg) and the solubility of CO_2 in orange essential oil (sl) at 323.15 K and 343.15 K as function of pressure.

T (K)	Orange essential oil—carbon dioxide		
	P (MPa)	sg (g/1000 g)	sl (g/g)
323.15	7.56	11.604	0.549
	8.11	11.766	0.978
	8.60	10.558	0.902
	8.70	11.326	0.828
	9.10	15.448	1.113
	9.60	20.728	2.218
343.15	10.14	16.079	0.614
	11.05	25.567	0.655
	12.14	45.086	0.861
	13.15	74.859	1.241

bility of the experimental data reported in this paper, values obtained from the empirical correlation can be used. In the comparison, however, it must be taken in to account that the composition of orange essential oil used in the work [12] is different from the one of the present work. In particular, in reference [12] the oil has a weight fraction of monoterpenes equal to 98.25% whereas a value of approximately 99% characterizes the oil in the present work. From the analysis of the figure we see that the data reported in this work are in agreement with data reported in reference [12], with relative mean deviations equal to 21% at 323.15 K and equal to 24% at 343.15 K

Figure 4 shows the solubility of CO_2 in the liquid phase, as a function of pressure. The solubility of the gas in the liquid phase increases with pressure and decreases with temperature, for the values of pressure and temperature are under investigation. At 323.15 K, an increase from approximately 0.5 to 2.2 g/g is observed, whereas the solubility increases from 0.6 to 1.2 g/g at 343.15 K. In **Figure 4** the comparison, of obtained experimental data with the empirical correlation of data [12] is reported: taking into account the considerations above discussed, the two data sets are in good agreement with relative mean deviations equal to 13% at 323.15 K and equal to 16% at 343.15 K.

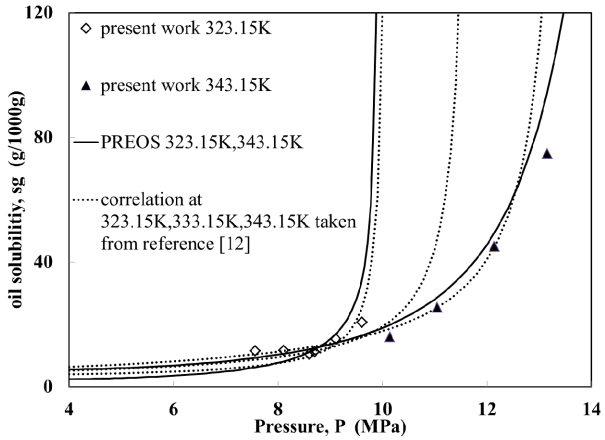

Figure 3. Experimental data presented in this work, literature data and model curve for solubility of orange essential oil in supercritical CO_2 at 323.15 K and 343.15 K as function of pressure.

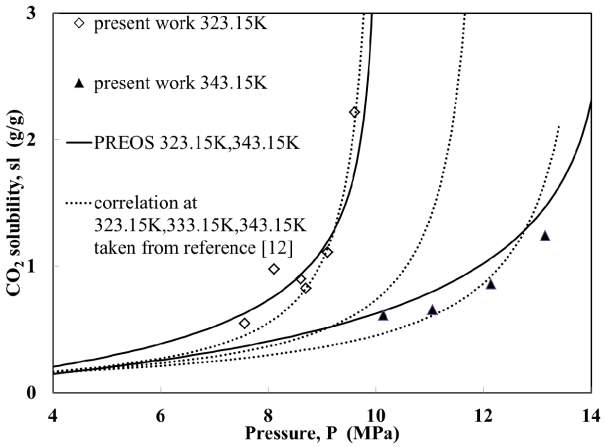

Figure 4. Experimental data presented in this work, literature data and model curve for the solubility of CO_2 in the oil phase at 323.15 K and 343.15 K as function of pressure.

The experimental data reported in **Table 2** can also be observed in the isothermal P-x-y diagrams reported in **Figure 5**, which represents the system as pseudo-binary (*i.e.*, considering orange essential oil as a pure component). The diagram provides an overview of the behavior of the system at the two temperatures. Each condition of equilibrium pressure and temperatures corresponds to a given value of the ratio oil/CO_2 used in the test. In fact, for a constant mass of oil, the added mass of CO_2 should be such as to reach the desired pressure in the apparatus (of fixed volume). Being the system not actually binary (*i.e.*, orange essential oil is not a pure compound), it follows that if another overall composition locus (for example by charging in the apparatus a mass of oil equal to 20 g instead of 30 g) is chosen, equilibrium P-x-y lines would change accordingly.

Table 3 shows the experimental compositions, on CO_2-free basis of phases in equilibrium at different values of temperature and pressure. The gaseous phase shows the enrichment in monoterpenes, on the contrary the liquid phase has only a modest enrichment in oxygenated terpenes and sesquiterpenes components. This behavior depends on the low value of the ratio solvent/feed utilized in the experimental runs: a minimal amount of oil is solubilized in the supercritical phase, and then the composition of the liquid phase is almost coincident with the one of the feed.

No literature experimental data are available for comparison because in the works [11,12] besides the monoterpenes, only a single "aroma" component is considered.

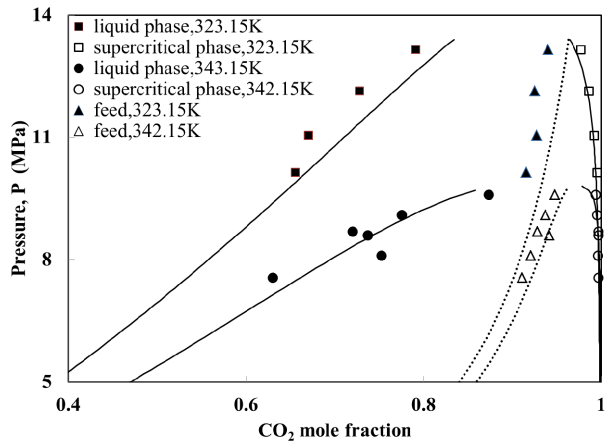

Figure 5. Pseudo-binary isothermal P-x-y diagrams at 323.15 K and 343.15 K.

From the analysis of experimental data it is apparent that the feed mass fraction values of the three classes of compounds are between the corresponding values in the gas and the liquid, and therefore mass balance of different components are respected. Some experimental runs (at 323.15 K and 9.1 MPa and 9.6 MPa; at 343.15 K and 11.05 MPa) show that both the supercritical and liquid phases are richer in monoterpenes than the feed. This problem is probably caused by some inaccuracies in the GC-analyses of this complex mixture.

In order to quantify this aspect, a selectivity of the solvent with respect to the separation of monoterpenes and oxygenated terpenes + sesquiterpenes compounds can be defined as follows:

$$S_{mt,ox} = \left(\frac{Y_{mt}}{X_{mt}}\right) \Big/ \left(\frac{Y_{ox}+Y_{st}}{X_{ox}+X_{st}}\right) \quad (1)$$

In Equation (1) Y_{mt}, Y_{ox} and Y_{st} indicate the weight fraction of monoterpenes , oxygenated terpenes and sesquiterpenes respectively in supercritical phase, whereas X_{mt}, X_{ox} and X_{st} indicate the mass fraction of the same components in the liquid phase.

From the data reported in **Tables 3**, not considering the above-mentioned experimental points showing inconsistencies in the mass balances, it can be seen that at 323.15 K the selectivity varies from 2 to 5.These values are higher than literature data [12] which vary from 1.1 to 3 in the same temperature and pressure ranges.

4. Thermodynamic Modeling

System Carbon Dioxide—Linalool

Equilibrium data of the system CO_2 linalool reported in **Table 1**, were represented by means of PREOS with the van der Waals mixing rules and two temperature-independent interaction parameters, as already reported in our previous works dealing with the thermodynamic characterization of systems composed by CO_2 and single component of lemon oil (limonene, citral and β-caryophyllene) [13-15].

Table 3. Experimental composition of supercritical and liquid phases (on solvent free basis).

T (K)	Orange essential oil compositions						
	P (MPa)	Xmt	Xox	Xst	Ymt	Yox	Yst
323.15	7.56	0.986	0.011	0.003	0.997	0.002	0.001
	8.11	0.990	0.009	0.001	0.997	0.002	0.001
	8.60	0.986	0.012	0.002	0.997	0.002	0.001
	8.70	0.987	0.011	0.002	0.997	0.002	0.001
	9.10	0.993	0.006	0.001	0.995	0.004	0.001
	9.60	0.993	0.006	0.001	0.994	0.005	0.001
343.15	10.14	0.990	0.009	0.001	0.997	0.002	0.001
	11.05	0.991	0.008	0.001	0.994	0.005	0.001
	12.14	0.986	0.012	0.002	0.994	0.005	0.001
	13.15	0,992	na	na	0.993	na	na

Attractive parameters (a_i) and covolumes (b_i) of CO_2 and linalool were calculated from critical properties and acentric factors through the relationships reported by Peng and Robinson [18]. To carry out these calculations, linalool critical parameters and acentric factor were determined by means of group contribution method [19]: the obtained values are reported in **Table 4** together with the one of CO_2. The relationships for the mixture attractive parameter and covolume are reported below:

$$a_m = \sum_{i=1}^{2}\sum_{j=1}^{2} z_i z_j \left[\sqrt{a_i a_j}\cdot\left(1-k_{ij}\right)\right] \quad (2)$$

$$b_m = \sum_{i=1}^{2}\sum_{j=1}^{2} z_i z_j \left[\frac{b_i+b_j}{2}\cdot\left(1-\eta_{ij}\right)\right] \quad (3)$$

In Equations (2) and (3) z_i and z_j indicate the mole fractions of the components in the generic phase (*i.e.*, gas or liquid) and k_{ij} and η_{ij} are the binary interaction parameters (both equal to zero if $i = j$ and $k_{ij} = k_{ji}$; $\eta_{ij} = \eta_{ji}$ if $i \neq j$).

The interaction parameters were calculated according to a well-defined procedure, by regression of experimental data, by minimizing of the follow objective function:

$$\Phi\left(k_{ij},\eta_{ij}\right) = \frac{1}{N_{50}}\sum_{i=1}^{N_{50}}\left(\left|\frac{y_{iC}-y_{iE}}{y_{iE}}\right| + \left|\frac{x_{iC}-x_{iE}}{x_{iE}}\right|\right) + \frac{1}{N_{70}}\sum_{i=1}^{N_{70}}\left(\left|\frac{y_{jC}-y_{jE}}{y_{jE}}\right| + \left|\frac{x_{jC}-x_{jE}}{x_{jE}}\right|\right) \quad (4)$$

In Equstion (4) y and x indicate the molar fraction in the gas and liquid phase, respectively, the subscript C stands for a quantity calculated by the thermodynamic model, the subscript E refers to experimental data, and N_{50} and N_{70} are the numbers of experimental data at respectively 323.15 K and 343.15 K. The average percentage deviation for the binary systems CO_2-linalool is 4.2%.

Besides representing the experimental data, **Figures 1** and **2** also show the equilibrium solubility curves calcu-

Table 4. Physical properties of CO_2 and components of orange essential oil

Compound	Physical property			
	MW	Pc (MPa)	Tc (K)	ω
carbon dioxide	44.01	7.376	304.2	0.225
limonene	136.24	2.788	651.17	0.389
linalool	154.25	3.155	646.03	0.6903
β-caryophyllene	204.36	2.076	736.15	0.518

lated with the optimal values of the temperature-independent interaction parameters that were determined in this work and the curves calculated by assuming $k = 0$ and e $\eta = 0$ (completely provisional values). In addition, **Figure 6** provides an overall view of the behavior of this binary system, at the two temperatures under investigation. Optimal values of interaction parameters were used also to correlate experimental data reported in reference [17] at 333.15 K (see **Figure 6**). The agreement seems to be satisfactory also with this set of experimental data.

The system CO_2-orange essential oil was modelized as composed of 4 components, which are CO_2 (the solvent) plus three selected main components representing the oil: the major monoterpene compound (*i.e.*, limonene), the major oxygenated compound (*i.e.*, linalool), and a sesquiterpene compound (*i.e.*, β-caryophyllene). Extensive discussion on this modeling approach is reported in other papers dealing with the modelization of the system CO_2-lemon essential oil [5]. The critical properties and acentric factor of limonene and β-caryophyllene are reported in **Table 4** whereas the values of interaction parameters for system CO_2-limonene and CO_2-β-caryophyllene taken from literature [10,15] are reported.

As for the binary-interaction parameters between oil compounds, meanings the sub-systems not involving CO_2, they were assumed equal to zero. On the whole, the complete set of values of the temperature-independent interaction parameters used for modeling the system CO_2-orange essential oil is reported in **Table 5**. It is here underlined that the only empirical parameters utilized by the thermodynamic model are the interaction parameters referred to binary sub-systems CO_2-orange essential oil components. Therefore, the model is predictive with respect to the multicomponent system.

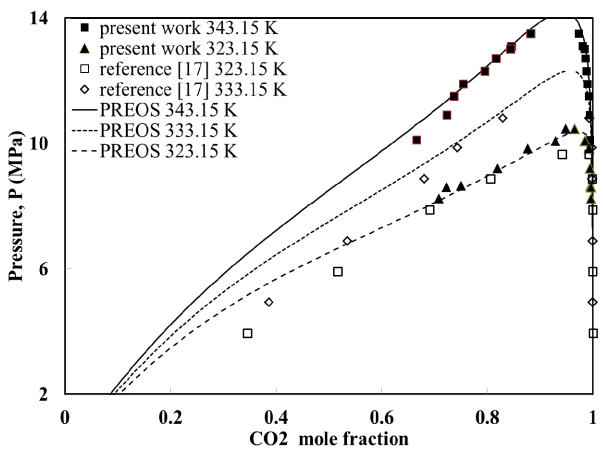

Figure 6. Experimental data presented in this work, data from reference [17] and equilibrium values obtained by means of PREOS at 323.15 K, 333.15 K and 343.15 K with k_{ij} and η_{ij} reported in Table 5.

The capability of the model of predicting the behavior of the system CO_2-orange essential oil was tested through a series of phase equilibrium calculations at constant pressure, temperature, and volume. In particular the volume of the apparatus (340 cm^3), the amount of loaded oil (30 g) and the oil composition (obviously in terms of limonene, linalool and β-caryophyllene representing monoterpenes, oxygenated compounds, and sesquiterpenes respectively) were fixed besides the values of pressure and temperature. By means of a specific software which takes into account the phase equilibrium equations (*i.e.*, isofugacity conditions) together with the mass balances and the volume constraint on the system, the amount and composition of the gas and liquid phases at equilibrium is provided as output. In particular, it is here noted that the amount of CO_2 in the system is an output parameter of the calculation.

Figures 3 and **4** show that the model correctly provides the solubilities in the gas and the liquid phases for the system CO_2-orange oil. Actually the model overestimates the solubility of CO_2 in the liquid phase at 343.15 K. The amount of CO_2 which is necessary to guarantee the specified pressure to be established is also very well predicted (see **Figure 5**). The capability of the model of providing a good representation of the pseudo-binary system is summarized in **Figure 6**, which shows calculated and predicted values of the mass fractions of the two phases in equilibrium.

The comparison between calculated and experimental values of equilibrium composition can also be carried out. In particular negligible values of relative deviation between calculated and experimental weight fraction of monoterpenes in liquid and supercritical phases are evaluated. On the contrary high values of the same deviations for oxygenated and sesquiterpenes weight fractions are obtained. These high deviations are due also to the inaccuracies of the CG analysis.

5. Conclusion

The gas-liquid phase equilibrium of the system CO_2-orange essential oil was experimentally determined in a constant-volume apparatus working at 323.15 K and 343.15 K, in the pressure ranges of interest for the deterpenation process. The experiments were carried out with an orange oil rich in monoterpenes (mt 99.05%, ox

Table 5. Binary interactions parameters for the systems CO_2-components of orange essential oil.

Interaction parameters	CO_2-limonene	CO_2-linalool	CO_2-β-caryophyllene
k_{ij}	0.089	0.016	0.089
η_{ij}	0.013	−0.069	−0.005
reference	[18]	this work	[X]

0,82%, st 0,13%). In the investigated pressure range, solubility of CO_2 in liquid phase and solubility of oil in the supercritical phase were determined. Furthermore, the composition of the gas and the liquid phase were determined, in terms of three main classes of components. A thermodynamic model based on PREOS, including van der Waals mixing rules corrected by two temperature-independent binary interaction parameters, was used in order to predict equilibrium data for the system CO_2-orange oil. The comparison is satisfactory because the model is capable of providing a good representation both of the experimental solubility data and the phases' compositions. The selected model is predictive with respect to the multicomponent system, being the regression parameters calculated only on data of selected binary subsystems.

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