High-Pressure phase equilibrium of the binary systems terpene oil-carbon dioxide

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Terpenes are an important group of compounds found in large amounts in plants. For the separation of their complex mixtures derived from natural sources, such as essential oils, supercritical carbon dioxide extraction would be of great interest to prevent thermal degradation of the product. Therefore, the design of supercritical CO_2 extraction process requires the knowledge of the phase equilibrium data**.**

This paper presents experimental equilibrium data for CO_2+p-cymene at temperature and pressures varying between 303-343 K and 6-15 MPa, respectively. The experimental data were obtained using a high pressure variable-volume view cell. The results were correlated with the Peng-Robinson equation using Van der Waals mixing rule and with several semiempirical methods.

1. Introduction

Terpenes are contained in essential oils and can be extracted from plant materials [1]. Its extraction is interesting because there are an important target market in food, perfumery and pharmaceutical industry.

Essential oils are traditionally obtained by steam distillation, but this technique can promote the degradation of thermolabile compounds. Besides, this process presents

several disadvantages, such as the formation of by-products, and important energy consumption, a low yield and a final product which contains solvent residue.

Separation by supercritical fluids is considered an alternative process because of low operating temperature and the complete removal of solvent. Design and development of supercritical fluid processes depends on knowledge about equilibrium between liquid and gases, because a solubility difference of several orders of magnitude can be achieved by an appropriate adjustment of pressure and temperature in the extractor [2]. By this reason, experimental data on high-pressure phase equilibrium are the basis of feasibility studies and process design in the field of supercritical fluid technology. Carbon dioxide is a suitable solvent for supercritical fluid extraction, due to its nontoxicity and low critical temperature, it can be used for extracting natural materials.

On one hand, high solubilities in CO_2 should be achieved, because in this way, lower CO_2 flow rates for the same extraction efficiency can be used, which reduce the installation costs. On the other hand, the CO_2 amount dissolved in the extract is of interest for the design of the separator, because this CO_2-extract mixture is expanded to atmospheric conditions. Normally, the gaseous CO_2 discharging from the expanded extract is vented to the atmosphere. Therefore, the liquid phase composition in the separator is responsible for one part of the CO_2 loss of a high-pressure extraction plant [3].

It is interesting to measure the equilibrium data in systems containing terpenes or other compounds with similar structure.

In this work, vapour-liquid phase equilibrium compositions of the binary system p-cymene/CO_2 at pressure ranging from 50-200 bar and temperature at 303.15, 323.15 and 343.15 K were measured. Experiments were carried out by the static analytical method, using a high pressure variable-volume cell. The experimental results obtained were

compared with previous data available in the literature [4] and were correlated using the Peng-Robinson equation of state (PR-EoS).

2. Experimental section

2.1. Materials

Carbon dioxide (99.8%) was purchased from Carburos Metálicos España S.A. (Madrid, Spain). p-Cymene (4-Isopropyltoluene) $\geq$ 97% pure was the selected terpenes supplied by Sigma-Aldrich and was used without further purification. Its structure is represented in Figure 1.
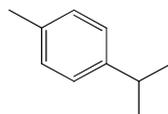
p-Cymene

Figure 1. Chemical structure of p-Cymene.

2.2. Equipment and experimental procedure

Experimental measurements were carried out using a high-pressure variable-volume cell (from Eurotechnica) as it is represented in Figure 2. The equipment consists of a variable-volume cell, supplied with a front and upper window and light for visual observation of phase separation. The cell has a maximum capacity of 50 cm^3 and contains a piston system, consisting in a manual pressure generator, a cylinder and a movable made of Teflon to avoid pressure drops only when samples are taken. The movable piston separates the equilibrium chamber from the pressurizing circuit. To allow a smooth displacement of the piston inside the cylinder, the piston was driven by the manual pressure generator and water was used as the pressurizing fluid. All the system is heated externally by an air bath made of Poly(methyl methacrylate) capable to resist temperatures up to 80ºC being the temperature inside the equilibrium chamber

measured by a thermocouple coupled to a digital led model testo 925 (Lenzkirch, Germany).
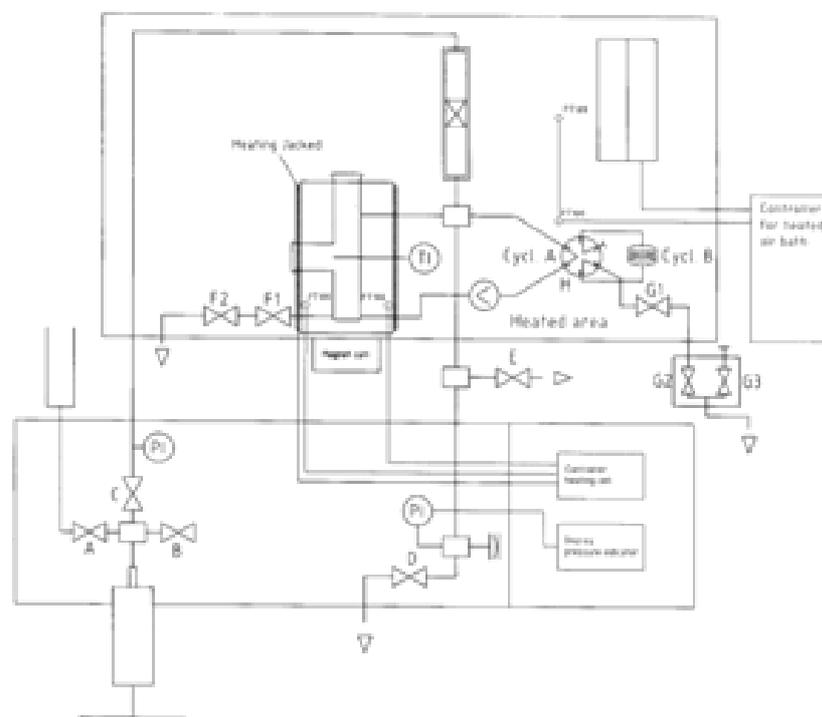

Figure 2. Experimental set-up employed to high-pressure phase equilibria measurements.

p-Cymene was introduced into the cell, and it was purged with CO_2 at low pressure to remove the residual air. Then, CO_2 was allowed to flow into the cell. Once the temperature was stabilized, the desired pressure was achieved, and the magnetic stirrer was turned on. After 12 hours, stirring was stopped, and the mixture was allowed to repose in order that phase segregation occurred.

Samples from the top and the bottom of the equilibrium cell were withdrawn using capillary lines and needle valves and decompressed to atmospheric pressure. Valves were thermostatized at the same temperature of the equilibrium cell. The manual pressure generator was employed to keep pressure constant during sampling (± 1 MPa) For the determination of the amount of CO_2, in the liquid phase, a sample was withdrawn from the bottom of the equilibrium cell and expanded into a glass vial, which

was weighted before and after sampling in a precision analytical balance with 0.0001 g accuracy . p-Cymene was collected in glass vials and separated from the CO_2 by using a trap. The amount of CO_2 was measured through a gas meter (model Ritter TG-05). Liquid samples were collected by triplicate and the uncertainty of the experimental CO_2 mass fraction was calculated as the average standard deviation (ADD).

The CO_2 density was calculated as a function of pressure and temperature with the equation of Bender.

3. Thermodynamic model

Although cubic equations of state (EoS) are simple, they are suitable for modelling hydrocarbon systems with light gases such as CO_2 over wide ranges of temperature and pressure, including subcritical and supercritical regions. Several authors showed that Peng-Robinson (PR) EoS can be used to describe the phase behaviour of carbon dioxide and terpene oils [3, 5-8].

The cubic equation of state calculates the properties of a fluid as if it consisted of only one component. If the fluid is a mixture, the parameters of the imaginary component must be calculated from the pure component parameters of the real components (Table 1), using mixing rules. The PR-EoS, coupled with the classical van der Waals mixing rule with one binary interaction parameter for the attraction parameter, is shown as follows:

$$P = \frac{R \cdot T}{V - b} - \frac{a}{V \cdot (V + b) + b \cdot (V - b)}$$

$$a = \sum_i \sum_j x_i \cdot x_j \cdot \sqrt{a_i a_j} \cdot (1 - k_{ij})$$

$$b = \sum_i \sum_j x_i \cdot x_j \cdot \left(\frac{b_i + b_j}{2}\right)$$

$$b = 0.07780 \cdot \frac{R \cdot T_c}{P_c}$$

$$a = 0.45724 \cdot \frac{R^2 \cdot T_c^2}{P_c} \cdot \left[1 + f\omega \cdot \left(1 - T_r^{\frac{1}{2}}\right)\right]^2$$

$$f\omega = 0.37464 + 1.54226 \cdot \omega - 0.26992 \cdot \omega^2$$

where P is the pressure, R is the gas constant, T is the temperature and V is the molar volume, ω is the acentric factor, k_{ij} is the binary interaction parameter which is evaluated using a iterative procedure by minimizing the objective function (OF) defined as:

$$OF = \frac{1}{N_y} \sum |y_{exp} - y_{calc}|$$

However, recent studies on the performance of conventional Equations of State, concludes that reliable representation of vapour-phase composition is hard to achieve, especially at near-critical conditions. By this reason, different semiempirical model, such as Chrastil [9], and Valle Aguilera[10] were chosen to represent equilibrium composition, furthermore, these equations need only the vapour phase composition.

Chrastil equation is based on the proposition that the association between solvent and solute molecules produces a solvate-complex gives a linear relationship between the logarithmic solubility and logarithmic density of pure CO_2.

$$\ln S = C_1 + \frac{C_2}{T} + C_3 \cdot \ln \rho$$

where S is the solubility, ρ is the pure CO_2 density (g/l), T is the temperature (K) and Ci are the constant correlated. Valle Aguilera proposed a modification by adding one new parameter to fit.

$$\ln S = C_1 + \frac{C_2}{T} + \frac{C_3}{T^2} + C_4 \cdot \ln \rho$$

4. Results

The experimental measurements on the gas-liquid equilibrium of the binary system carbon dioxide (1)/p-cymene (2) were performed at 303.15, 323.15 and 343.15 K. The phase equilibrium was determined for several pressure values, in the range of 40-170 bar. Table 1 shows the experimental vapour-liquid equilibrium data for the CO_2/p-cymene system at different temperatures; the values are typically averages of three measurements.

As it is observed, solubility of p-cymene in the supercritical phase and the solubility of CO_2 in the liquid p-cymene rich phase increase with pressure. This may be due to the increase of CO_2 density with increasing pressure, since CO_2 density is directly related to the dissolving power [12].

Table 1. Experimental data on vapour-liquid equilibrium in the system CO_2/p-Cymene.

T(K)	P (MPa)	x_{CO_2}	y_{CO_2}	S (mg /g CO_2)
303.15	5.94	0.36748	0.99872	3.96305
303.15	6.45	0.38789	0.99439	17.36933
303.15	7.63	0.46075	0.99946	1.67191
303.15	9.83	0.61048	0.99939	1.88864
303.15	10.2	0.62518	0.99923	1.45518
303.15	11.79	0.76465	0.99834	5.13959
303.15	12.81	0.87565	0.99770	7.12111
323.15	4.17	0.13525	0.99151	26.28620
323.15	5.67	0.19003	0.98985	31.42578
323.15	6.47	0.24478	0.98771	38.05152
323.15	8.10	0.30509	0.99785	6.65669
323.15	9.49	0.45933	0.99591	12.66320
323.15	9.95	0.53488	0.99509	15.20203
323.15	12.08	0.67414	0.99491	15.75933
323.15	12.62	0.72357	0.99458	16.78106
323.15	13.04	0.77838	0.99262	22.84949
323.15	15.75	0.82495	0.99106	27.67946
323.15	16.22	0.85657	0.98948	32.57135
343.15	6.05	0.12570	0.99947	1.64095
343.15	7.81	0.15240	0.99941	1.82672
343.15	8.82	0.23463	0.99914	2.66268
343.15	9.35	0.30455	0.99901	2.44595
343.15	10.07	0.35221	0.99834	5.13959
343.15	12.42	0.55323	0.99813	5.78978
343.15	12.87	0.58528	0.99802	6.13035
343.15	15.54	0.84283	0.99764	7.30688

Figure 3 shows a general comparison between the p-Cymene solubility data reported by Wagner and Pavlíček [4] and the new data measured in this work.
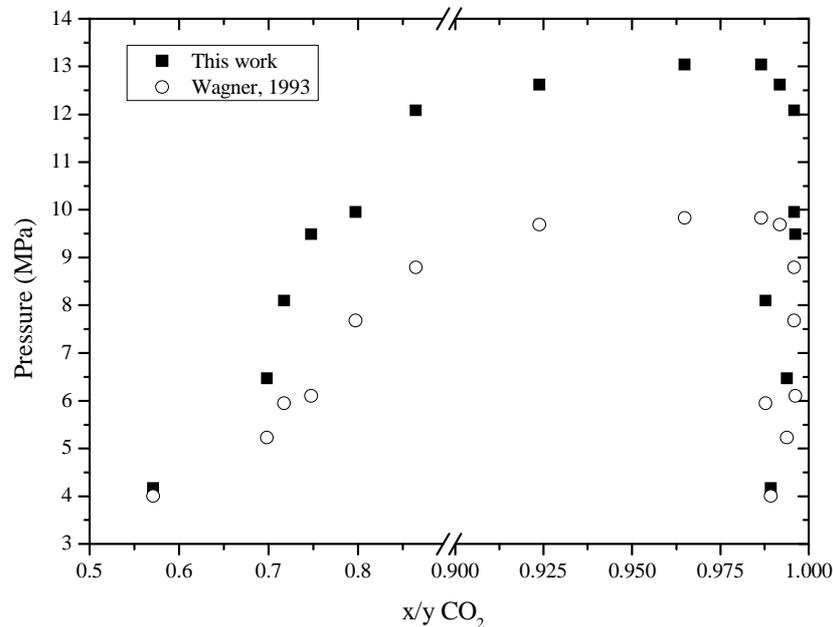

Figure 3. Phase behaviour of the carbon dioxide/p-Cymene system at 323.15 K

In order to model the high-pressure phase equilibrium of the system carbon dioxide/p-Cymene, the Peng-Robinson EoS with the classical mixing rules was successfully employed by several authors to correlate experimental data of terpene oils [6, 8, 13, 14]. The regression of experimental data was carried out defining as the objective function the minimum of the error between the calculated and the experimental data of vapour and liquid phases. The critical constants and acentric factors of the pure components were taken from Reid and col. [15] and are listed in Table 2.

Table 2. Critical properties and acentric factors of pure components.

	Tc (K)	Pc (MPa)	ω
CO_2	304.12	7.374	0.225
p-Cymene	652.00	3.050	0.376

The optimised values of the interaction parameters k_{12} at different temperatures are collected in Table 3.

Table 3. Optimised k_{12} values of carbon dioxide (1) and p-Cymene (2).

T(K)	k_{12}
303.15	0.08556
323.15	0.09182
343.15	0.12915

As it was previously explained, semiempirical equations were proposed to correlate equilibrium data. The optimal parameters for Chrastil and Valle Aguilera equations are shown in Table 4.

Table 4. Optimised C_1, C_2 and C_3 for carbon dioxide and p-Cymene.

Equation	C_1	C_2	C_3	C_4
Chrastil	-153.06	50730	11.768	-
Valle Aguilera	26.252	-10730	2.6683	1.1311

Figure 4.a shows the results obtained using Chrastil and Valle Aguilera correlations. Figure 4.b represents the experimental solubility values versus the calculated ones observing that in this case, Valle Aguilera equation represents slightly better the solubility behaviour.
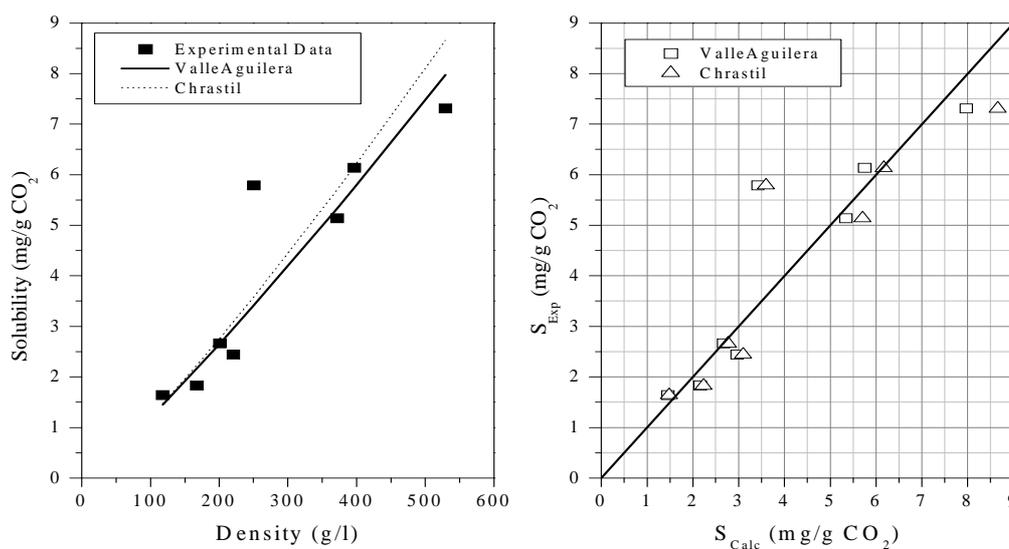

Figure 4. a. Experimental solubility vs. Density. b. Experimental Solubilities vs. Calculated.

Acknowledgments

References

1. Reverchon, E., L. Sesti Osseo, and D. Gorgoglione, *Supercritical CO2 extraction of basil oil: Characterization of products and process modeling.* The Journal of Supercritical Fluids, 1994. **7**(3): p. 185-190.
2. Richter, M. and H. Sovová, *The solubility of two monoterpenes in supercritical carbon dioxide.* Fluid Phase Equilibria, 1993. **85**(C): p. 285-300.
3. Gamse, T., Marr, R., *High-pressure phase equilibria of the binary systems carvone-carbon dioxide and limonene-carbon dioxide at 30, 40 and 50ºC.* Fluid Phase Equilibria, 2000. **171**: p. 165-174.
4. Wagner, Z., Pavlíček, J., *Vapour-liquid equilibrium in the carbon dioxide- p-cymene system at high pressure.* Fluid Phase Equilibria, 1993. **90**: p. 135-141.
5. S.A.B. Vieira de Melo, G.M.N.C., A.M.C. Uller, F.L.P. Pessoa, *Modeling high-pressure vapor–liquid equilibrium of limonene, linalool and carbon dioxide systems.* Journal of Supercritical Fluids, 1999. **16**: p. 107-117.
6. Akgün, M., N.A. Akgün, and S. Dinçer, *Phase behaviour of essential oil components in supercritical carbon dioxide.* Journal of Supercritical Fluids, 1999. **15**(2): p. 117-125.
7. Oliveira, A.L., et al., *Modelling of high-pressure phase equilibrium in systems of interest in the food engineering field using the peng-robinson equation of state with two different mixing rules.* Journal of Food Process Engineering, 2010. **33**(SUPPL. 1): p. 101-116.
8. Vieira de Melo, S.A.B., et al., *Modeling high-pressure vapor-liquid equilibrium of limonene, linalool and carbon dioxide systems.* Journal of Supercritical Fluids, 1999. **16**(2): p. 107-117.
9. Chrastil, J., *Solubility of solids and liquids in supercritical gases.* Journal of Physical Chemistry, 1982. **86**(15): p. 3016-3021.
10. del Valle, J.M. and J.M. Aguilera, *IMPROVED EQUATION FOR PREDICTING THE SOLUBILITY OF VEGETABLE OILS IN SUPERCRITICAL CO//2.* Industrial and Engineering Chemistry Research, 1988. **27**(8): p. 1551-1553.
11. Manuel Budich, G.B., *Vapor–liquid equilibrium data and flooding point measurements of the mixture carbon dioxide+orange peel oil.* Fluid Phase Equilibria, 1999. **158**: p. 759-773.
12. Paulaitis, M.E., et al., *SUPERCRITICAL FLUID EXTRACTION.* Reviews in Chemical Engineering, 1983. **1**(2): p. 179-250.
13. Iwai, Y., et al., *Entrainer Effect of Ethanol on High-Pressure Vapor−Liquid Equilibria for Supercritical Carbon Dioxide + Limonene + Linalool System.* Journal of Chemical & Engineering Data, 2005. **50**(6): p. 1844-1847.

14.   Gironi, F. and M. Maschietti, *High-pressure gas-liquid equilibrium measurements by means of a double-chamber recirculation apparatus. Data on the system carbon dioxide-limonene at 50 and 70 °C.* The Journal of Supercritical Fluids, 2010. **55**(1): p. 49-55.

15.   Reid, R.C., J.M. Prausnitz, and B.E. Poling, *The properties of gases and liquids.* 1987.