PHASE EQUILIBRIUM MEASUREMENTS FOR THE CLOVE OIL + CO$_2$ SYSTEM

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Phase equilibria data for the clove oil + CO$_2$ system were measured at pressures of 58.32 to 108.06 bar and temperatures of 303.15, 313.15, and 328.15 K. The phase equilibrium experiments (cloud points) were performed in a high-pressure variable-volume view cell. The apparatus consists basically of a view cell with two sapphire windows for visual observations. The equilibrium cell contains a movable piston, which permits the pressure control inside the cell. Phase transitions were recorded visually, as bubble or dew points, varying the pressure behind the piston using the syringe pump and CO$_2$ as pressurizing fluid. The clove oil used in the present work was extracted with carbon dioxide at 150 bar and 298.15 K and consisted of a mixture of the following substances were detected: eugenol, ß-caryophyllene, a-humulene and eugenol acetate. Liquid-liquid-vapor (303.15 K $\pm$ 1 K) and liquid-vapor equilibriums were observed (313.15 K and 328.15 K $\pm$ 1 K)

Keywords: Phase equilibrium, clove oil, carbon dioxide

INTRODUCTION

Supercritical fluid extraction from solids, especially from aromatic, medicinal, and spice plants is an important technology due basically to its classification as a green technology and its capability of extracting valuable substances at middle temperatures. Nonetheless, in spite of the observed reduction in the investments costs, the manufacturing costs of SFE extracts is still considered prohibitive by several entrepreneurs. The investments costs have decrease as a result of its growing knowledge during the past decade. In order to achieve a reduction in manufacturing costs, it is mandatory to gather all the information related to a particular system. From this point of view, the knowledge of phase equilibria can benefit design of SFE system specifically in the separation step. Though, relevant data have being published in literature on phase equilibria of several binaries and ternary systems of interest, for process design it is more appropriate the use of phase equilibria measured for the real systems.

The purpose of the present work was to measure the phase equilibria data for the clove oil + CO$_2$ system, using clove oil obtained by SFE at 150 bar and 298.15 K.

MATERIALS AND METHODS
Preparation and characterization of the clove oil

Clove oil was obtained by supercritical CO$_2$ extraction in a Spe–ed System (Applied

Separations, Allentown, USA). A Thar Designs 300 mL extraction column (Pittsburgh, USA, with internal volume of 250 mL) was used to obtain clove oil extract. In this column was added 201.51 g of clove bud particles. The Extraction was conducted at 150 bar, 25 °C, and CO_2 flow rate of 4.25 g/min. The extraction time was 1.5 hours and the total yield was 14.9 %. This experiment was repeated in order to have enough amount of clove oil to conduct the phase equilibrium experiments.

The analysis of the clove oil obtained by supercritical CO_2 extraction was done by GC-FID (Shimadzu, GC 17A, Kyoto, Japan) equipped with a capillary column DB-5 (30 m x 0.25 mm x 0.25 µm, J&W Scientific, USA) and split injector. The analysis conditions used was given by Rodrigues et al [1]. The quantitative analysis used the external standard method [2]. The quantification was done using a standard of eugenol (Sigma, Lot: 17H0239, 97.0 % of purity) β-caryophyllene (Sigma, Lot: 38H2503, 98.6 % of purity) and α-humulene (Sigma, Lot: 97H2505, 98.8 % of purity). The amount of eugenol acetate was obtained by the mass balance since there was no standard and the chromatogram presents only for peaks.
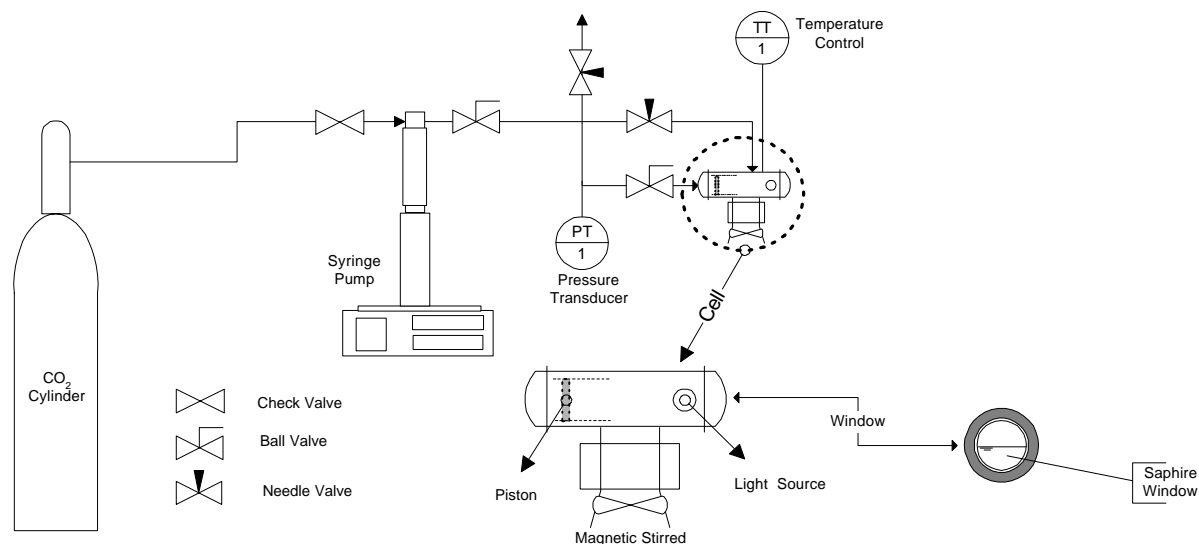
The thermophysical properties of the pure components were estimated using the method of Constantinou and Gani [3], and the acentric factor with the Lee and Kesler method [3].

Phase equilibria apparatus and procedure

Phase equilibrium experiments (cloud points) were performed through a static method without sampling [4], in a high-pressure variable-volume view cell. The apparatus is very similar to the one used in a previous study and has been extensively tested to orange peel oil/CO_2 and polymer/hydrocarbons systems [5], [6]. Thus, only a brief description is given. A schematic diagram of the apparatus is presented in Figure 1. The apparatus consists of a view cell with two sapphire windows for visual observations, an absolute pressure transducer (Smar, model LD 301, Sertãozinho-SP, Brazil), with a precision of ±0.120bar, a portable programmer (Smar, model HT 201, Sertãozinho-SP, Brazil) for the pressure data acquisition and a syringe pump (ISCO, model 500D, Lincoln, NE, USA). The equilibrium cell has a maximum internal volume of 25cm^3 and contains a movable piston, which permits the pressure control inside the cell. Phase transitions were recorded visually as bubble or dew points just varying the pressure behind the piston by using the syringe pump and CO_2 (99.9% purity, AGA) as pressurizing fluid. The cell is equipped with an electrical heater and a PID controller (DIGI MEC, model SHM 112, São Paulo-SP, Brazil). The controller is connected to a thermocouple, which is in direct contact with the fluid mixture inside the cell body. This arrangement provided a temperature control with a precision of 0.5 K.

Initially the cell and all lines were flushed with low-pressure CO_2 to remove residual air. Depending on the desired global composition, an amount of solute (clove oil) was weighed on a high precision scale (Ohaus Analytical Standard, ± 0.0001g, São Paulo-SP, Brazil) and loaded into the cell. Then, the solvent was pumped into the cell in order to reach the pre-established global composition. The amount of solvent charged was monitored by the change in the total volume of the transfer vessel of the pump. Then, the cell content was kept at continuous agitation with the help of a magnetic stirrer and a Teflon-coated stirring bar. After reaching the desired temperature, cell pressure was increased by applying pressure on the back of the piston with the syringe pump until observation of a single phase. At this point, the system was allowed to stabilize at least 30 minutes and the cell pressure was decreased slowly until incipient formation of a new phase. The equilibrium pressure was then recorded, after repetition of the experimental procedure at least three times, leading to an average

reproducibility around of 0.70 bar. After completing the test at a given temperature, the cell temperature was stabilized at a new value and the experimental procedure was repeated. Experimental data were measured at 303.15, 313.15, and 328.15 K.

Figure 1: Experimental apparatus: high-pressure variable-volume view cell

RESULTS AND DISCUSSION

Table 1 shows the composition of the clove oil and Table 2 the calculated thermophysical properties. The chemical structures of the compounds are shown in Figure 2.

Table 1: Composition of the Essential Clove Oil

Component	Mass Fraction	Molecular Mass (kg/kmol)	Molar Fraction
Eugenol	0.755	164.20	0.794
ß-caryophyllene	0.121	204.36	0.102
a-humulene	0.014	204.36	0.012
Eugenol Acetate	0.110	206.24	0.092

Table 2: Properties of the Pure Components of the Clove Oil

Component	$T_{boiling}$, K	$T_{critical}$, K	$P_{critical}$, bar	$V_{critical} \times 10^3$, m³/kmol	?
Eugenol	545.07	763.20	33.42	500.90	0.6545
ß-caryophyllene	519.23	714.73	18.98	701.30	0.4799
a-humulene	524.50	719.00	17.09	743.00	0.4502
Eugenol Acetate	556.92	767.01	22.97	668.10	0.5735

Using the molar fractions (Table 1) and thermophysical properties (Table 2) the properties of the clove oil were calculated using the Kay's rule [2]. The properties of the pseudo binary system are in Table 3.

(a)

(b)

(c)

(d)
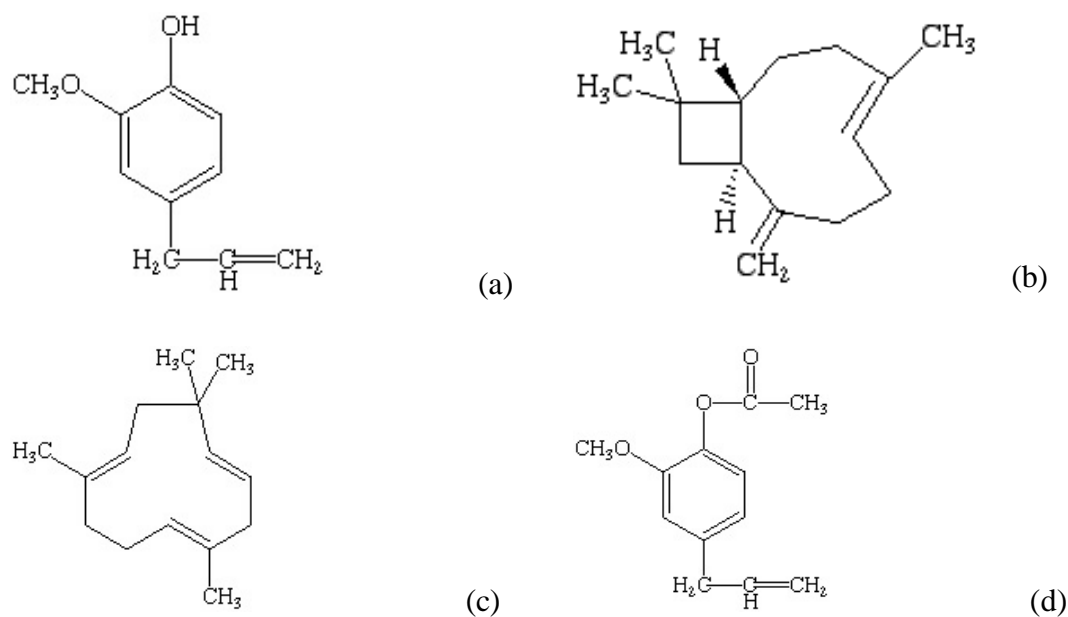
Figure 2: Pure compounds present in clove oil: (a) eugenol, (b) ß-caryophyllene, (c) a-humulene, (d) eugenol Acetate.

**Table 3: Critical Proprieties of the dioxide carbon and the pseudo compound**

| Components	$T_{critical}$, K	$P_{critical}$, bar	ω	MM, kg/kmol
CO_2	304.21	73.83	0.2236	44.01
Clove Oil	758.33	30.97	0.6286	172.02

The equilibrium data at 303.15, 313.15, and 328.15 are in Figures 3 to 5. At 303.15 K transition liquid–liquid–vapor was observed while at 313.15 and 328.13 K only liquid–vapor transition was observed.
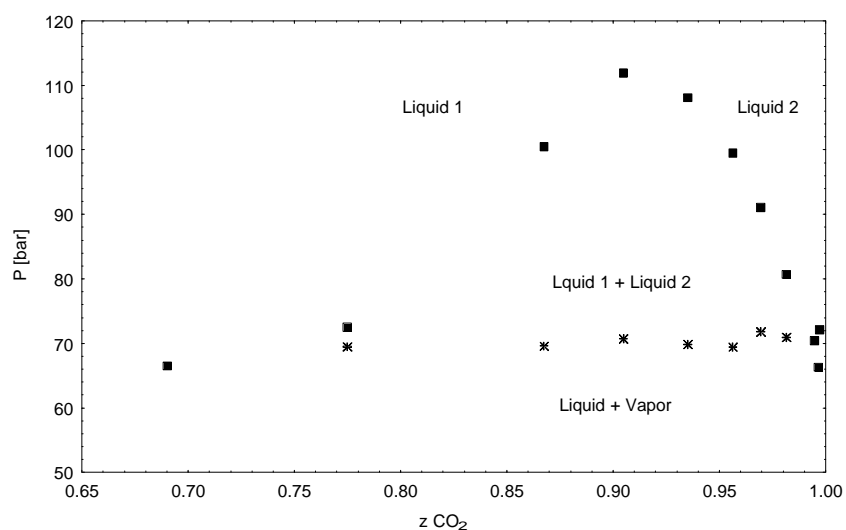
Figure 3: experimental phase diagram for the clove oil + CO_2 system at 303.13 K.
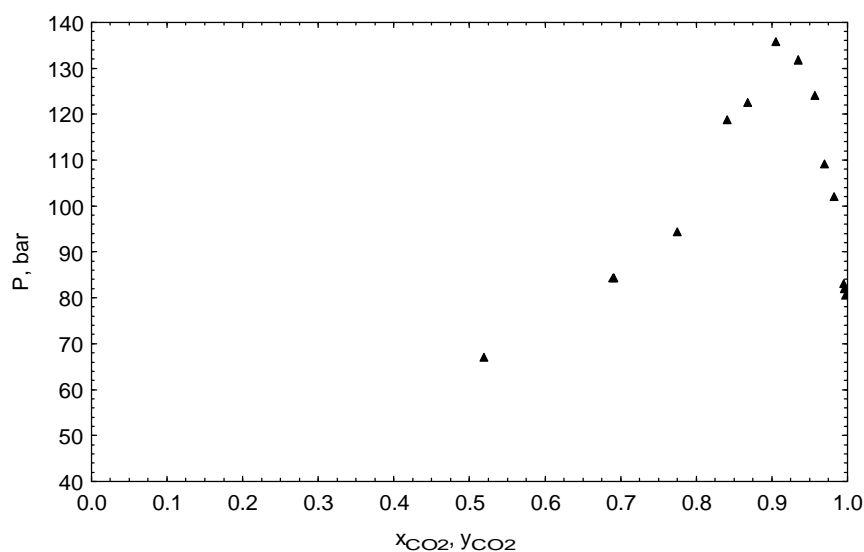
Figure 4: Experimental phase diagram for the clove oil + CO₂ system at 313.13 K.
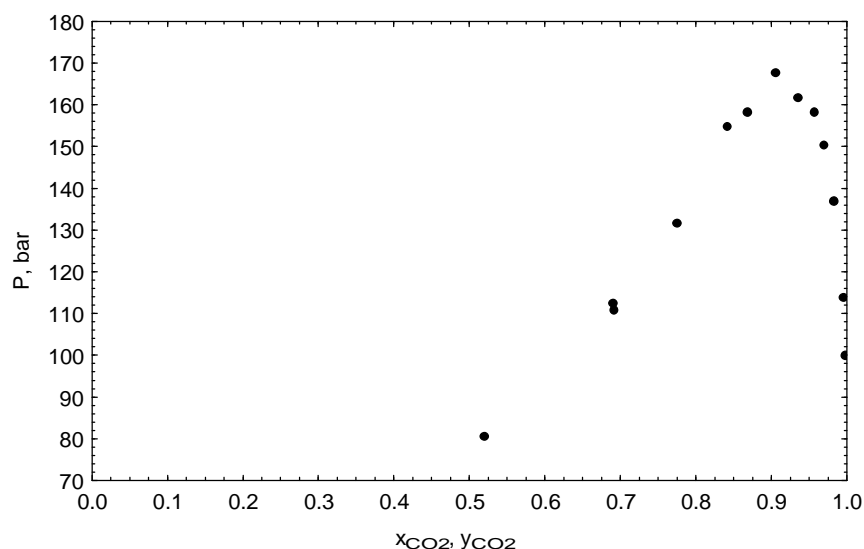
Figure 5: Experimental phase diagram for the clove oil + CO₂ system at 328.13 K.

The equilibrium data of eugenol in supercritical CO_2 was presented by Cheng et al. [7] for temperatures of 308.15, 318.15, and 328.15. The values of pressure obtained at 328.15 and by x_{CO2} of 0.51 and 0.70 were 84 and 125 bar, respectively. These values are a little Comparing these values with the ones obtained for the clove oil they are larger

CONCLUSIONS

In this work, the equilibrium data of clove oil in supercritical CO_2 for temperatures of 303.13, 313.13, and 328.13 K were presented. The system at lower temperature showed the presence of two liquid phases in equilibrium with the vapor phase while the other systems had only one liquid phase in equilibrium with the vapor phase.

ACKNOWLEDGMENTS

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