PHASE TRANSITIONS OF BINARY AND TERNARY SYSTEMS WITH CARBON DIOXIDE, TRIGLYCERIDES AND ETHANOL

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This work reports phase equilibrium experimental data at high pressures for systems formed by carbon dioxide with ethanol and triglycerides. Phase equilibrium experiments were carried out using the static synthetic method in a high-pressure variable-volume view cell in the temperature range of 20–70°C up to 270bar, for binary carbon dioxide-triglycerides and ternary carbon dioxide-triglycerides-ethanol systems at various overall compositions. Phase equilibrium P-T and P-x diagrams were constructed allowing the identification of fluid-liquid transitions. A very intriguing phase behavior has been found at high carbon dioxide concentrations, which seems to be an U-LCST pressure transition curve.

INTRODUCTION

The possibility of using a much less pollutant fuel when compared to diesel from petroleum and producing many chemical raw materials for food, pharmaceutical and cosmetic industries has motivated the biotransformation of vegetable oils, some of them in excess in the world market from almost native growing plants, to result in high-value added products or drastic reduction in environmental investments. Potential applications of supercritical fluid technology in fats and oils processing have been extensively studied over the last two decades [1, 2]. Carbon dioxide, either as an expanded liquid or as a supercritical fluid ($SCCO_2$), may be a viable replacement for a variety of conventional organic solvents in enzyme-catalyzed reaction systems because it is a nonflammable, nontoxic solvent, inexpensive and readily available in high purity. Recently, numerous studies have shown that many enzymatic reactions can be advantageously conducted with $SCCO_2$ over organic solvents, resulting in much higher rates and selectivity [3, 4, 5, 6]. To conduct such reactions at high pressures, the knowledge of phase behavior of the reaction constituents is of primary importance if we take into account enzyme inactivation, maximization of desired products production through reactants partition coefficients and the obvious need of a homogeneous phase for enzyme-substrates interaction. Experimental pressure transition data of binary and ternary system containing soy bean oil, castor oil, ethanol and carbon dioxide are reported and discussed in this work.

MATERIALS AND METHODS

Material

The commercial soy oil used in this work is a mixture of five triglycerides (Table 1) while the castor oil is constituted almost exclusively by triricinolein (97%).

Table 1: Composition of soil bean oil.

Triglycerides	Composition (wt%)
Tripalmitin	11.39%
Tristearin	2.48%
Triolein	24.33%
Trilinolein	53.00%
Trilinolenin	8.80%

Apparatus

The experimental apparatus used in this study is described in detail elsewhere [7]. Phase equilibrium experiments (cloud points) were carried out in a high-pressure variable-volume view cell. The apparatus consists basically of a view cell with three sapphire windows for visual observations, an absolute pressure transducer (Smar LD 301), with a precision of $\pm$ 0.012 MPa, a portable programmer (Smar, HT 201) for the pressure data acquisition and a syringe pump (ISCO 260D). The equilibrium cell contains a movable piston, which permits the pressure control inside the cell. Phase transitions were recorded visually through manipulation of pressure, using the syringe pump and the solvent (carbon dioxide) as pressurizing fluid. The experimental apparatus employed to conduct the experiments up to 270 bar and 70°C is depicted in Figure 1.
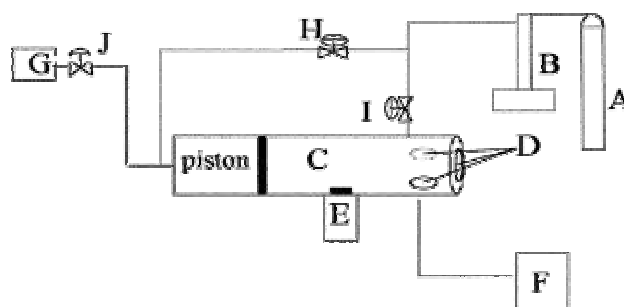
Figure 1: Schematic diagram of phase equilibrium apparatus: A, CO_2 cylinder; B, syringe pump; C, equilibrium cell; D, sapphire windows; E, magnetic stirrer; F, white light source; G, pressure transducer; H, ball valve; I, micrometering valve; J, relief valve.

Procedure

Depending on the desired global composition, an amount of vegetable oil and ethanol was weighed on a high precision scale balance (with 0.0001g accuracy) and loaded into the cell. Afterwards, 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 mass of the transfer vessel of the pump. During the charging process no pressure was applied behind the piston to ensure that the experiments were started with the cell at its maximum volume. 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 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 four times, leading to an average reproducibility 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.

RESULTS AND DISCUSSIONS

Figures 2 and 3 show the PT diagram for CO_2-castor oil-ethanol system, for two different ethanol-oil molar ratio (q), at various carbon dioxide global compositions. Figure 4 is a PT diagram of soybean oil-CO_2 system at three different carbon dioxide compositions. As expected, rising q the bubble pressures transition of the ternary system drops to lower values. For all systems investigated the pressure transition is strongly affected by the global composition of carbon dioxide. At relatively high CO_2 concentrations and temperatures close to the carbon dioxide critical temperature, the pressure transition values decrease with increasing temperature. For the ternary system, an increase of q induces a lowering of CO_2 concentration for which this behavior appears. Such behavior may be interpreted as a fluid-liquid U-LSCT transition that results from two antagonic phenomena. The first leads to a decrease of the pressure transition with increasing temperature. This transition type is referred to as Upper Critical Solution Temperature and is a consequence of differences in interaction energy between carbon dioxide and oil molecules. The second phenomenon appears at high temperatures as a result of the difference in the coefficient of thermal expansion between solvent and vegetable oil. The resulting pressure transition curve is labeled as Lower Critical Solution Temperature (LCST). Figure 5 is a P-T diagram of CO_2-ethyl-ricinoleate (biodiesel from castor oil) system. The U-LCST behavior emerges at carbon dioxide concentrations well above those observed in others systems investigated in this work. For the same carbon dioxide concentration, the pressure transition of CO_2-ethyl ricinoleate system is less than those observed in ternary and other binary systems.
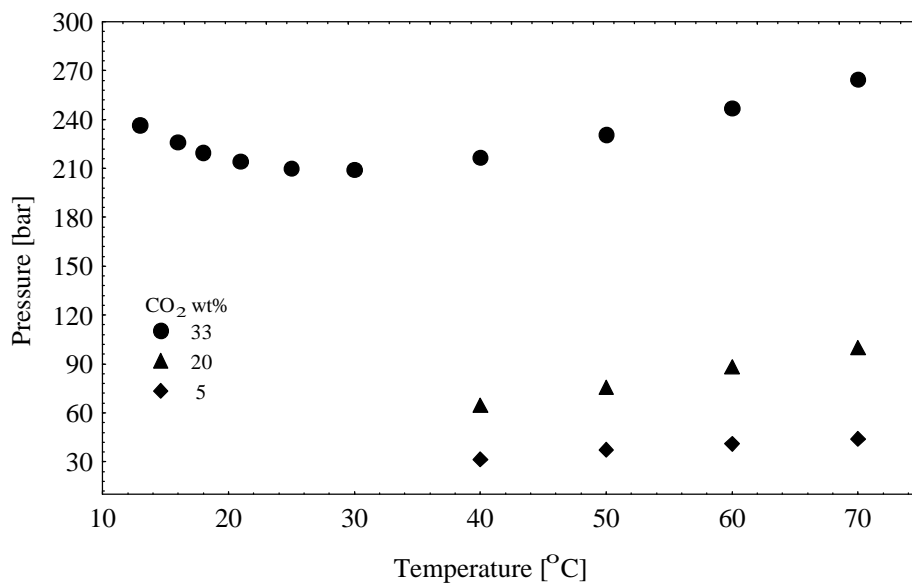
In addition to P-T diagrams, phase behavior is often represented in pressure-composition space. Figures 6 and 7 are P-x diagrams are CO_2-castor oil and CO_2-ethyl ricinoleate systems.
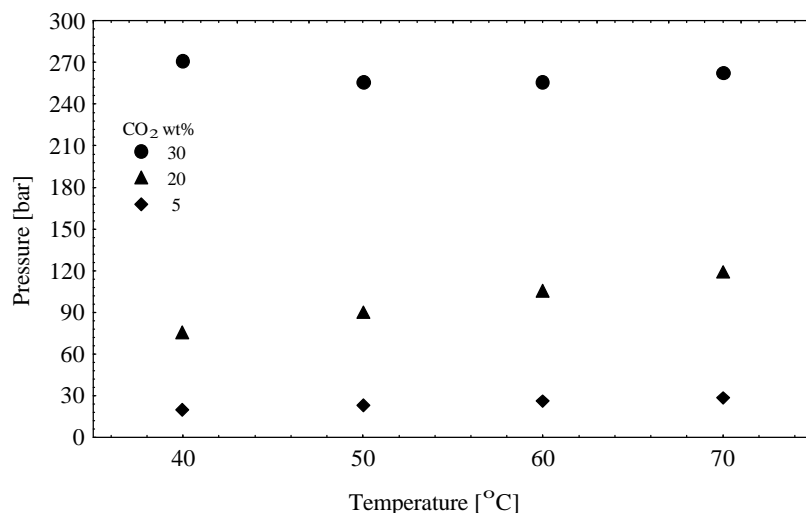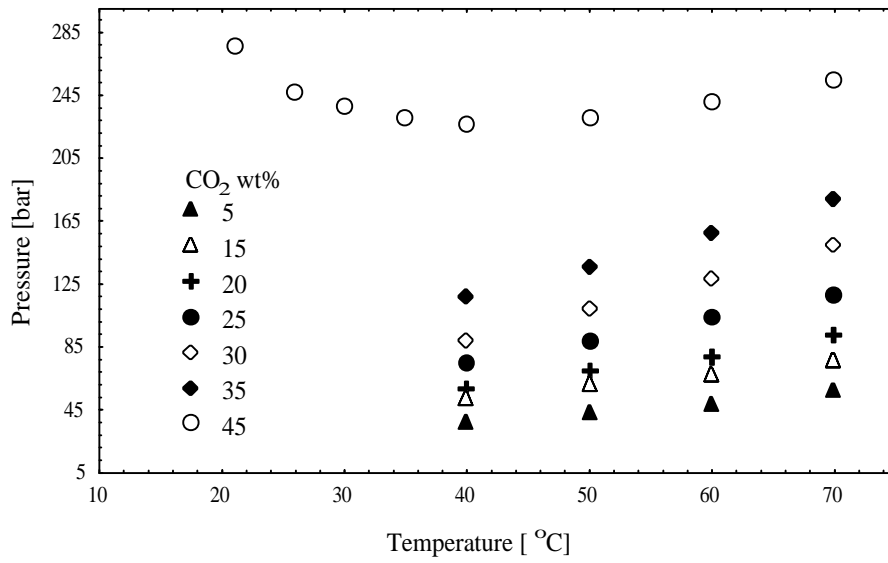

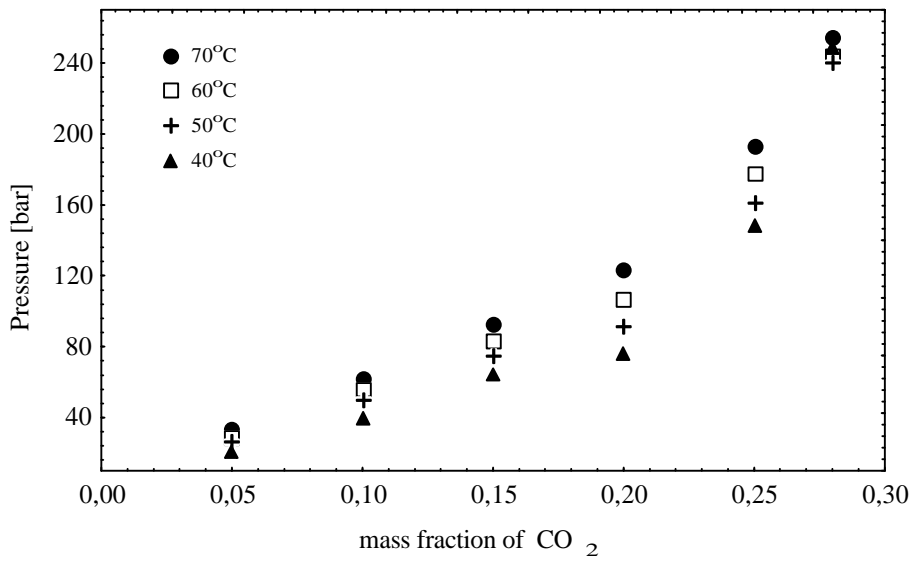**Figure 2:** P-T diagram for CO_2-castor oil-ethanol system with q = 1.
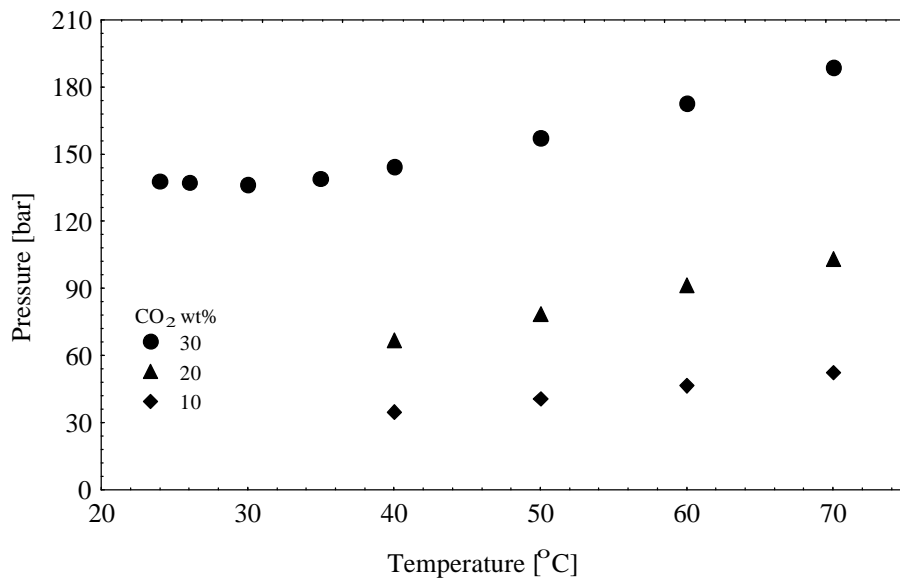
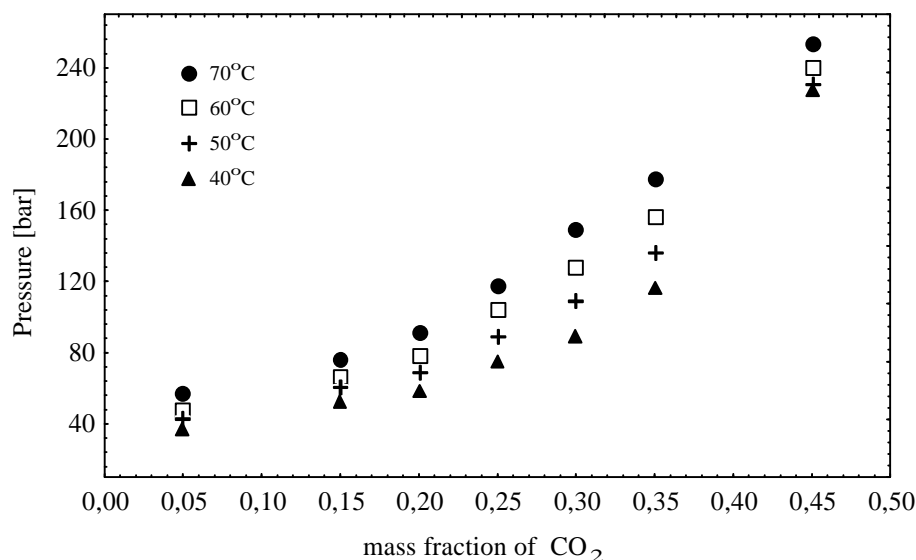**Figure 3:** PT diagram for CO_2-castor oil-ethanol system with q = 3.

Figure 4: PT diagram for CO_2-soy bean oil system.

Figure 5: P-T diagram for ethyl-ricinoleate-CO_2 system.

Figure 6: P-x diagram for CO_2-castor oil system.

Figure 7: P-x diagram for CO_2-ethyl ricinoleate system.

CONCLUSION

Phase behavior of ternary and binary systems formed by vegetable oils, ethanol and carbon dioxide was investigated in this work. Results show that the pressure phase transtion is strongly affected by carbon dioxide concentration and by the ethanol-oil molar ratio. The appearance of a similar U-LCST transition curve at relatively high carbon dioxide concentrations is somewhat an intriguing phenomenon and needs more investigation. Modeling of these systems can be performed by the use of a moleculary based model such as Statistical Associating Fluid Theory (SAFT) which takes into account the relative high asymmetry between components.

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