LIQUID-LIQUID-SUPERCRITICAL FLUID MODELING FOR SYSTEMS CONTAINING CARBON DIOXIDE, PROPANE AND TRIGLYCERIDES

P.Hegel, G.Mabe, M.Zabaloy, S.Pereda and E.A.Brignole*
PLAPIQUI, Universidad Nacional del Sur - CONICET
CC 717, 8000 Bahía Blanca, ARGENTINA

*ebrignole@plapiqui.edu.ar

Abstract: The use of mixed near critical solvents (CO_2 + propane) for vegetable oil extraction process presents the advantage of the good solvent capacity of propane together with a non-flamable vapor phase due to the CO_2 content. With the aim to design and optimize this process, in a previous work, we obtained vapor-liquid-liquid experimental data for the system CO_2 + propane + sunflower oil [1]. The modeling of phase equilibria of this near critical solvents with triglycerides using the GCA-EOS model has been studied in several works [3,4], however this model is not able to correctly predict, using the available group binary interaction parameters, the liquid – liquid – vapor region for mixtures of carbon dioxide and propane with triglycerides. In this work, we present new experimental phase equilibria data on the binary and ternary systems including CO_2, propane and triacetin, which will be useful to correctly asses the interaction parameters of CO_2 and propane with the triester group (TG) of the oil molecule. Liquid CO_2 is completely miscible with triacetin and the addition of propane increases the liquid immiscibility of this ternary mixture, this is the opposite behavior presented by mixtures with long chain triglycerides, in which the addition of CO_2 increases the liquid immiscibility.

INTRODUCTION

In a previous work [1] we reported vapor-liquid-liquid experimental data for the system carbon dioxide + propane + sunflower oil and vapor-liquid data for the system carbon dioxide + sunflower oil. Liquid or supercritical carbon dioxide is immiscible with vegetable oils and has very low solvent power for the extraction of fixed oils. The previous work on phase equilibria of carbon dioxide + propane + vegetable oil mixtures was motivated for the interest of extracting fixed oils in the region of complete miscibility of the oil with the solvent and in a range of carbon dioxide concentrations that render a non flammable vapor phase. The selection of optimum extraction conditions requires the phase equilibrium modeling of these mixtures under liquid – liquid - vapor and liquid – vapor equilibria.

The modeling of phase equilibria of near critical solvents with triglycerides using the GC-EOS model [2] has been studied in several works [3,4], however the model predictions of the liquid – liquid – vapor region for mixtures of carbon dioxide and propane with triglycerides, using the available group binary parameters were in error when compared with the experimental data. For instance, Florouse et al [5] have studied the modeling with the GC-EOS of the phase equilibria of carbon dioxide with a series of triglycerides using the GC-EOS model. These authors reported that they can not represent the behavior of carbon dioxide with triacetin (a small triglyceride) using the same set of parameters used for the larger triglycerides. In this regard, it is interesting to look at experimental infinite dilution activity coefficient (γ^∞) data of alkanes in triacetin. Bermudez et al [6] reported γ^∞ for hexane and heptane in triacetin: 9.28 and 11.24, respectively. We can see that the alkanes form highly non ideal solutions in triacetin and these binaries may exhibit liquid – liquid equilibria at room temperature. Therefore experimental studies on liquid – liquid equilibria of alkanes with triacetin where carried out in the present work. This fact is pointing to the need of additional experimental information to revise the interaction between the main binary groups of this type of systems: triester group (TG), paraffinic (CH3, CH2), olefinic (CH2=CH2) groups with the carbon dioxide and propane (molecular) groups. In

previous works [3,4], the triester group TG is defined as: [(CH₂COO)₂CHCOO)]. However in this work a new (molecular) group [(CH₂COO)₂CHCOO) (CH3)₃] is used for triacetin (AAA). The vegetable oil is also represented by a single pseudo-triglyceride with the following molecular structure: $(CH2)_n (CH2=CH2)_m [(CH_2COO)_2 CHCOO) (CH2)_3]$, where the values of m and n are obtained from the fatty acids composition of the oil. Table 1 shows the new molecular pure group, and table 2 shows the binary interaction parameters between triacetin, propane and CO_2. The other GC-EoS group and interaction energy parameters used in this work are those of Espinosa et al. [4].

Table 1. Pure group molecular triacetin parameters (AAA: triacetin)

Group	T*(K)	Q	g*	g'	g''
AAA	704.3	6.492	297558.55	-1.94625	0.0

Table 2. Binary interaction parameters used in this work to model phase equilibria in systems of triacetin with CO_2 and propane

I	J	kij*	kij'	αij	αji
AAA	CO_2	1.0000	0.0000	0.0000	0.0000
AAA	Propane	0.905	0.0000	0.0000	0.0000

In previous studies [1] on carbon dioxide + propane + triglycerides, carbon dioxide played the role of an antisolvent leading to phase split and liquid – liquid immiscibility of the solvent mixture with the triglyceride at high carbon dioxide concentrations. In the case of mixtures with triacetin, the carbon dioxide and propane solvent behaviour are reversed, since carbon dioxide is completely miscible with triacetin but triacetin is only slightly miscible in propane. Therefore in a ternary system propane plays now the role of an antisolvent. Liquid–liquid–vapor equilibrium experimental studies for this ternary are reported in the present work.

MATERIALS AND METHODS

The mutual solubility data of triacetin + hexane were obtained at 20ºC using a liquid - liquid equilibrium glass cell. By carefully sampling each phase and evaporating the hexane in a vacuum stove, the molar fraction composition of the hexane and triacetin phases were determined.

The mutual solubilities of the binary propane + triacetin and the phase equilibria of the ternary propane + carbon dioxide + triacetin mixtures, were determined in a windowed variable volume equilibrium cell (Fig.1). The equilibrium cell has a movable piston that is used to control the cell pressure through volume changes, and to keep the pressure constant while sampling. In this cell it is possible to withdraw samples from up to three phases (liquid-liquid-vapor). The composition of oil in the heavy and light liquid phases was determined gravimetrically, the amount of solvent (propane + carbon dioxide) in the liquid phases was determined volumetrically and the composition of the solvent in each of the three phases by gas chromatography. Details of the experimental apparatus and technique are given by Hegel et al [1]. The experiments of propane + triacetin were carried out over the liquid-liquid-vapor equilibrium line and also at liquid-gas conditions in a range of temperatures between 308 and 353 K. In the ternary system CO2+propane+triacetin the lowest temperature was set at 293.15K and the highest was chosen as 313 K. The experimental error compositions in the heavy phase are in the order of 1-3 %, however in the light phase the error in the triacetin weight fraction is of the order of 10% due to the small amount of triacetin in the light phase. Above 333 K the cell was used as a constant volume cell because it was the maximum operating temperature of the Polypak seals. Under this situation it was not possible to sample the light phase without having a rather large change in the system pressure.

Bubble pressures of the binary CO_2+triacetin and the ternary CO_2 + propane + sunflower oil mixtures under conditions of complete miscibility were carried out also in the windowed variable volume equilibrium cell. The static method used in this work is described elsewhere [8], [9].

The bubble pressure measurements were made for mixtures of constant global composition. The experimental oil weight composition for the ternary systems CO2+propane+sunflower oil varied between 20 and 44% and carbon dioxide composition between 8 to 20 wt%. The error in liquid composition was evaluated in 1.5-2 % in oil weight fraction. Duplicate measurements of bubble points at each temperature were made to check the reproducibility of the technique.

The bubble points for the binary system CO_2+triacetin were measured for a range of compositions of carbon dioxide between 27 and 78 (weight %), at temperatures between 293 and 323 K.
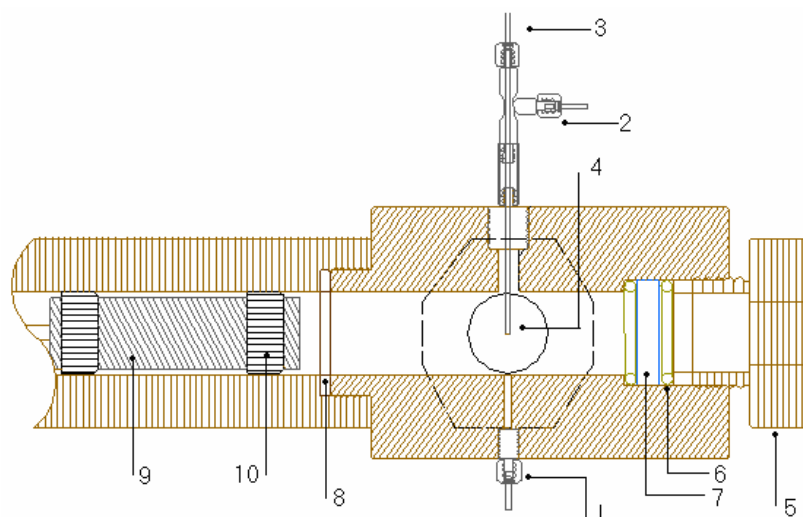

Figure 1 Variable volume equilibrium cell: 1. Heavy liquid phase sample. 2 vapor phase sample. 3 light liquid phase sample. 4 line of liquid phase sample. 5 view support. 6 O-ring seal. 7 view glass. 8 washer. 9 piston. 10 polypak seal.

RESULTS

Liquid – Liquid – Vapor Equilibria for Triacetín + low molecular weight alkanes

Table 3 reports the experimental results of liquid-liquid equilibria for the system triacetin + hexane at 293 K. The strong immiscibility between hexane and triacetin is also depicted in figure 2 for the binary triacetin + propane.

Table 3. Experimental mutual liquid solubilities for hexane + triacetin at 293 K

	Hexane phase	Triacetin phase
Weight fraction of hexane (%)	96.1	5.474
Weight fraction of triacetín (%)	3.895	94.52

Figure 2 reports the compositions of the liquid-liquid-vapor equilibria in a pressure vs. composition diagram as a function of temperature, and the GC-EOS correlation for the system propane + triacetin according to the interaction parameters reported in table 2. The system propane + triacetin has liquid - liquid immiscibility up to the propane critical temperature and thereafter offers liquid – gas immiscibility. This gas – liquid immiscibility will be observed up to very high temperatures as predicted by the GC-EOS model. Therefore the propane + triacetin binary is a Type III system in the classification of van Konynenburg and Scott [7].
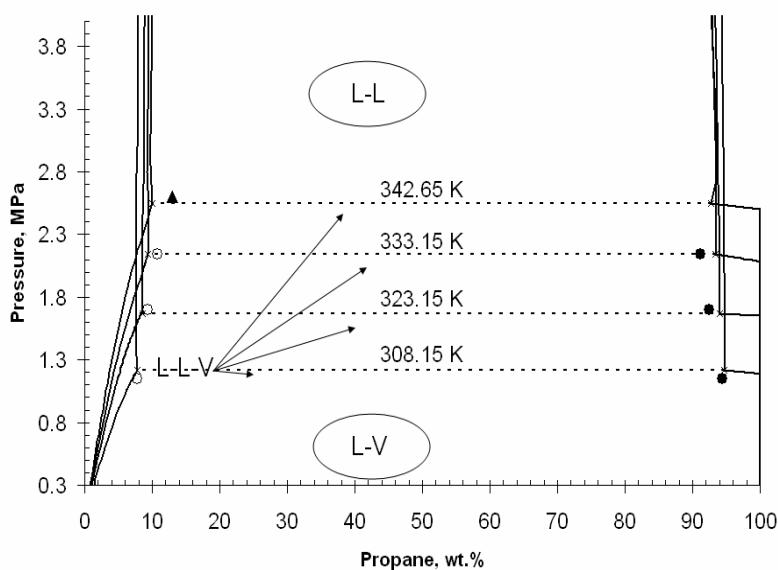
Figure 2 Propane + triacetin phase equilibria. Liquid –liquid - vapor equilibria. (Lines) GC-EOS model prediction:
(○) Experimental L1 phase composition: variable volume equilibrium cell.
(▲) Experimental L1: Fixed volume equilibrium cell.
(●) Experimental L2 phase composition.

Bubble Points of the System Carbon Dioxide + Triacetín

The main purpose of these studies was to obtain experimental information on the interaction between the triglyceride group "AAA" and carbon dioxide to improve the correlation and prediction of phase equilibria of carbon dioxide with fats and vegetable oils. The experimental results are represented in figure 3 together with GC-EOS predictions. According to GC-EOS predictions, the pressure vs. temperature behavior, for different CO_2 concentrations, indicates complete miscibility of triacetin with carbon dioxide in the liquid phase for all mixture compositions lower than 60wt.% of triacetin. For higher concentrations of triacetin the GC-EOS models predicts partial miscibility in the liquid phase, however it has not been observed experimentally. This is a quite different behavior with respect to the CO2 with triglycerides with long hydrocarbon chains, like fats or vegetable oils for which liquid phase immiscibility persists over a certain composition range even at high pressures and temperatures. It is clear that this information will be very valuable to obtain a more realistic parameterization of the group contribution equation of state thermodynamic model (GC-EOS)
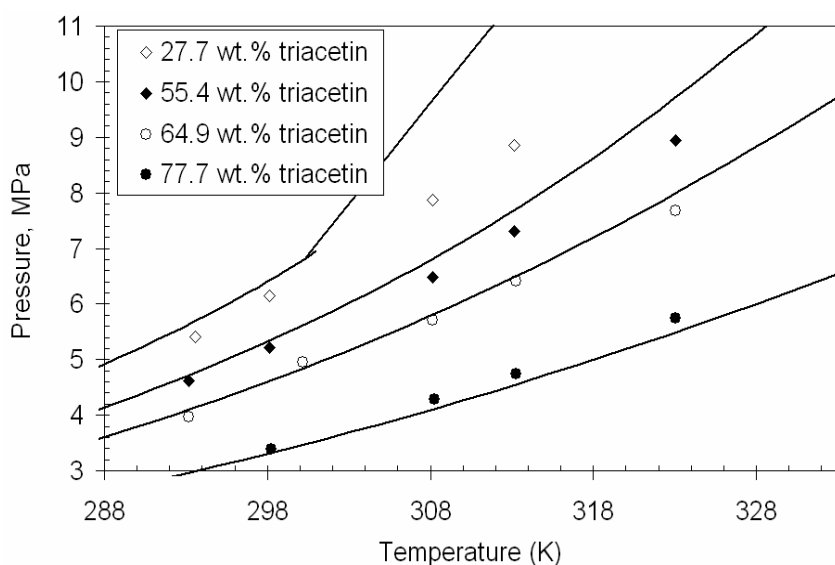

Figure 3 Bubble points of CO_2 + triacetin. (Lines) GC-EOS model predictions.

Liquid – Liquid – Vapor Equilibria for the Systemc Carbon Dioxide + Propane   + Triacetín

The LLV region of this system was studied at two temperatures: 298.5 K and 308.3 K. The experimental results are given in Table 4. In this case the heterogeneous region decreases at constant temperature with the increase of carbon dioxide concentration i.e higher   pressures.

Table 4. L_1 L_2 V equilibria for the system CO_2 + propane   + triacetin

| P	T	L_1			L_2			V		
MPa	K	CO_2	C_3H_8	Triacetin	CO_2	C_3H_8	Triacetin	CO_2	C_3H_8	Triacetin
1.15	308.3	0.000	0.078	0.922	0.00	0.944	0.056	0.000	1.00	*.*
1.89	308.3	0.045	0.096	0.860	0.107	0.861	0.031	0.256	0.744	*.*
3.27	308.3	0.128	0.131	0.741	0.270	0.605	0.125	0.607	0.393	*.*
4.00	308.3	0.209	0.150	0.641	-	-	-	0.635	0.365	*.*
4.29	308.3	0.252	0.185	0.563	0.375	0.381	0.244	0.672	0.328	*.*
4.63	308.3	0.296	0.200	0.504	0.402	0.352	0.245	0.706	0.294	*.*
2.01	298.5	0.078	0.099	0.823	0.174	0.765	0.061	0.521	0.479	*.*
3.03	298.5	0.174	0.138	0.688	0.317	0.517	0.165	0.654	0.346	*.*
3.23	298.5	0.211	0.145	0.644	-	-	-	0.632	0.368	*.*
4.50	298.5	0.440	0.179	0.381	-	-	-	0.774	0.226	*.*
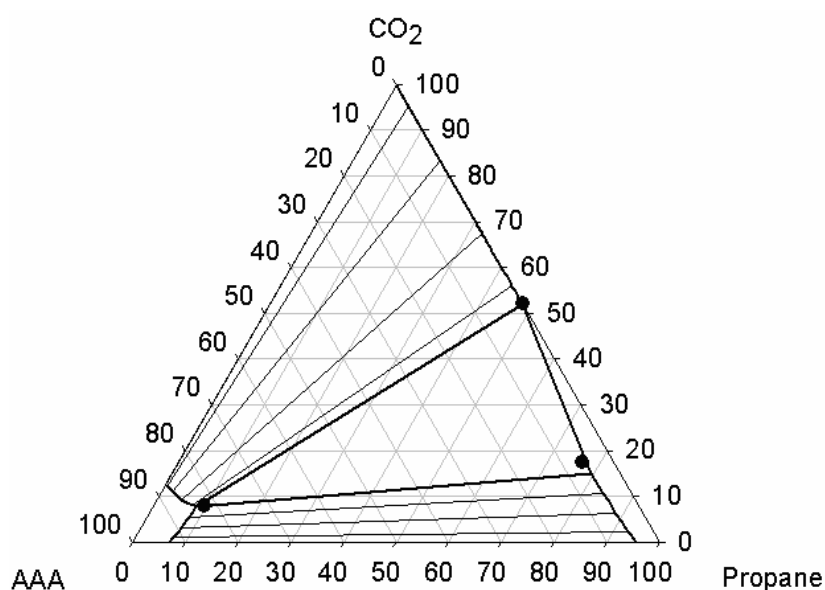
Figure 4 Liquid-Liquid-Vapor Equilibria for the system CO_2 + propane + triacetin at 298.5 K and 20.1 bar. (●) Experimental liquid – liquid - vapour compositions. (lines) GC-EOS predictions.

Figure 4 shows the experimental liquid-liquid-vapour equilibria at 298.5 K and 2.1 MPa, and the GC-EOS prediction of the ternary system. It can be observed that the GC-EOS prediction agrees well with the experimental data.

Bubble Points of the System Carbon dioxide + propane   + Sunflower Oil

The experiments with the ternary system CO_2 + propane + sunflower oil were intended to cover the bubble pressure as a function of temperature from ambient temperature to the temperature of incipient liquid phase split at the bubble pressure condition. Figure 5 shows the bubble pressures for two global

compositions studied as a function of temperature. The composition of carbon dioxide has the strongest effect on the system vapor pressure. When the composition of carbon dioxide goes from 8.29 to 17.8 weight % there is a clear difference in the temperature at which the liquid phase became heterogeneous. The bubble points prediction of GC-EOS model agrees well with the experimental phase equilibria, as can be observed in figure 5.
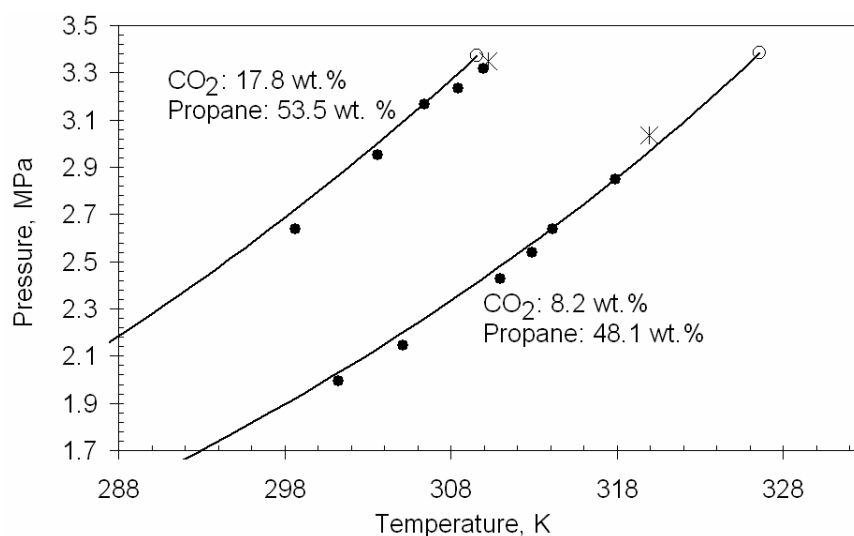

Figure 5 Bubble points of the system CO_2-Propane-Sunflower Oil. (●) Experimental liquid-vapor bubble point. (∗) Experimental liquid-liquid-vapor bubble point. (−) GC-EOS liquid-vapor bubble point prediction. (○) GC-EOS liquid-liquid-vapor bubble point prediction.

CONCLUSIONS

The experimental results of vapor-liquid and liquid-liquid equilibria of the present work for the system propane + triacetin indicate a highly non ideal behaviour for this system that depicts liquid-liquid immiscibility over a wide range of conditions of pressure and temperature. This phase behaviour is completely different of the one of propane with long chain triglycerides that depicts a type IV global phase behaviour with regions of complete miscibility in the liquid and propane supercritical region. The opposite is found for carbon dioxide that has complete miscibility with triacetin under liquid-vapor equilibrium conditions. However, CO_2 has strong immiscibility with long hydrocaron chain triglycerides. The new experimental information is be very valuable for the parameterization of a group contribution thermodynamic model for the representation of phase equilbria over a wide range of molecular weight of triglycerides in mixtures with carbon dioxide and propane.

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