

# PHASE BEHAVIOR OF BINARY SYSTEMS OF CARBON DIOXIDE AND CERTAIN LOW-MOLECULAR WEIGHT TRIGLYCERIDES: MEASUREMENTS AND THERMODYNAMIC MODELING

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This contribution reports on the fluid phase behavior of binary mixtures of carbon dioxide and four saturated triglycerides: triacetin, tributyrin, tricaproin and tricaprylin. The objective of this work is to analyze the effect of the triglyceride molecular weight on the phase behavior of mixtures with carbon dioxide. The experimental work covers a temperature range between 276 K and 368 K and pressures up to 15 MPa. The mixtures with tributyrin, tricaproin and tricaprylin show liquid-liquid immiscibility near the critical point of pure carbon dioxide. No liquid-liquid phase split was observed in mixtures with triacetin, the triglyceride lowest in molecular weight. The fluid phase behavior of these systems was modeled with the group contribution equation of state GC-EoS. The equation was able to describe vapor-liquid, liquid-liquid and vapor-liquid-liquid equilibria, with a single set of group interaction parameters.

## INTRODUCTION

Vegetable oils are valuable natural products; they consist mainly of triglycerides, with approximately 10% diglycerides, a small fraction of free fatty acids and a number of minor components (sterols, tocopherols, phospholipids, etc.) that have added value as pharmaceuticals and food additives.

Distillation is not a suitable separation process for vegetable oils because degradation of the triglycerides may easily occur at the operational temperatures required. The presence of solvent residues, inherent to solvent extraction, is also becoming increasingly unacceptable in products to be used for human consumption. In that respect, hexane is a significant example of a widely used extraction solvent that will be abandoned in the very near future. Solvents like hexane are also highly inflammable and for that reason these solvents should be avoided, if possible. Consequently, an alternative fractionation technique, not suffering from these shortcomings would be most advantageous.

Supercritical gas extraction is such an alternative technique. An important advantage of this technique is that the solvent power of supercritical fluids (SCF) can be manipulated by small variations in either pressure or temperature. The near-critical solvent is easily recovered from the extract and from the extraction residue due to its high volatility. In comparison with liquid solvents, supercritical fluids also have high diffusivities, low

densities, and low viscosities, allowing mass transfer processes and phase separations to occur rapidly.

Supercritical fluids are particularly effective for the isolation of thermally unstable compounds of low volatility because separation can be accomplished at moderate temperatures. For this reason supercritical fluid extraction is being considered as an alternative technique to extract and fractionate vegetable oils (Eggers et al. 1985; Friedrich et al. 1982; Klee et al. 1986). Supercritical carbon dioxide, which is both nonflammable and nontoxic, is considered to be a substitute for hexane (Bamberger et al., 1988).

The first reported commercial process using supercritical fluids for the fractionation of lipids was the Solexol process developed by the M. W. Kellogg Co. in 1947 (Passino, 1949; Dickinson and Meyers, 1959). In this process supercritical propane was used to extract and fractionate edible oils. Six plants were built to refine fish oil, animal fat, and vegetable oils (Bamberger et al., 1988).

For apparent reasons, knowledge of the phase behavior of relevant triglyceride + SCF systems is a prerequisite in order to be able to select adequate process conditions. Experimental measurements on these systems not only provide quantitative insight into their general phase behavior, but in addition, important information can be withdrawn for the thermodynamic modeling.

It is the aim of this experimental and modeling study to provide insight into how the fluid phase behavior of binary systems of carbon dioxide with triglycerides changes systematically with molecular weight. For that purpose, the binary fluid phase behavior of carbon dioxide with a series of saturated triglycerides (triacetin, tributyrin, tricaproin and tricaprylin) was investigated. Triacetin is the first member of the triglyceride family and it has three  $\text{CH}_3$  methyl radicals attached to the triglyceride backbone. In the remaining triglycerides, the length of each aliphatic chain increases in two  $\text{CH}_2$  radicals; i.e. in comparison with triacetin, there are 6 extra  $\text{CH}_2$  radicals in tributyrin, 12 in tricaproin and 18 in tricaprylin.

## EXPERIMENTAL

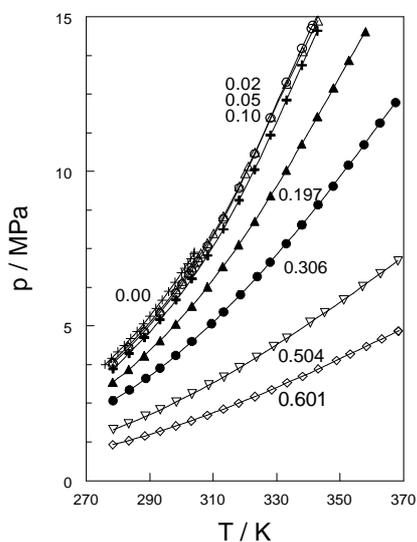
The Cailletet apparatus used for performing the phase equilibrium experiments, operates according to the synthetic method. At any desired temperature, the pressure is varied for a sample of constant overall composition until a phase change is observed visually. Details of the apparatus and experimental procedures can be found elsewhere (Raeissi and Peters, 2001).

Carbon dioxide (99.995 vol%) was supplied by Hoek-Loos and was used without further purification. The supplier of triacetin was Fluka and a purity of > 99% was claimed. The purity of all triglycerides was better than 99 mol %.

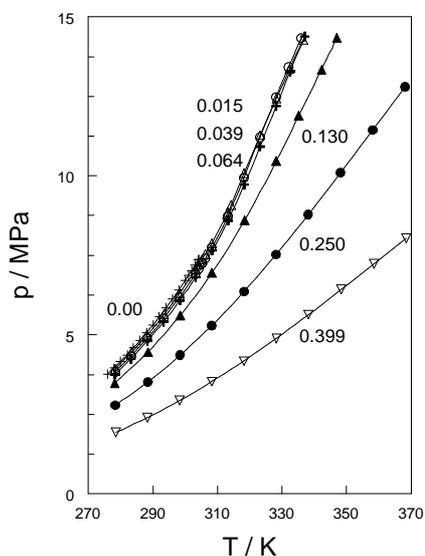
## EXPERIMENTAL RESULTS

Figures 1-4 represent the primary experimental data obtained for the binary systems between  $\text{CO}_2$  and each one of the four triglycerides. The data are presented as isopleths, which is the way they have been obtained experimentally. From these data isothermal  $p,x$ -diagrams can be derived straightforwardly.

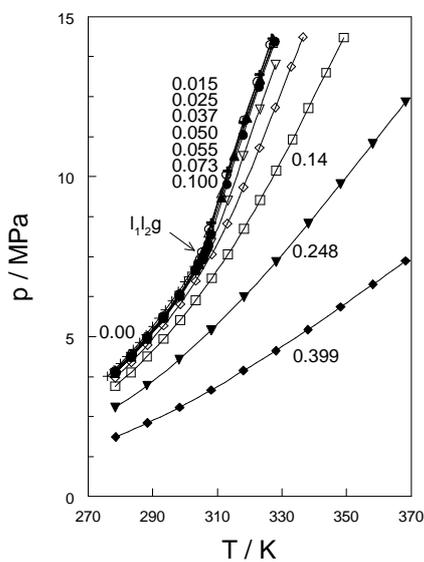
The system  $\text{CO}_2$  + triacetin does not show liquid-liquid immiscibility, whereas the remaining binaries do. A three-phase liquid-liquid-vapor ( $l_1l_2g$ ) locus could be established in  $\text{CO}_2$  + tricaproin and  $\text{CO}_2$  + tricaprylin binaries, with a critical endpoint of the nature



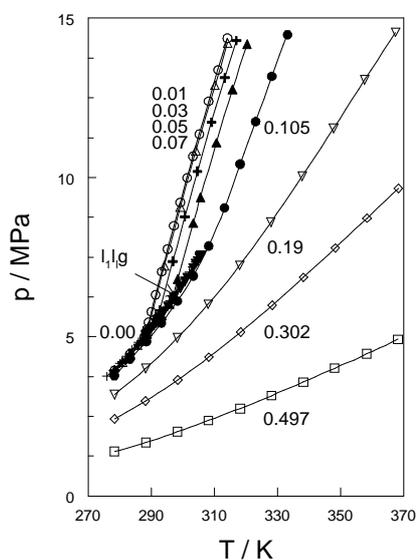
**Figure 1.** Experimental isopleths of the system  $\text{CO}_2$  + triacetin: symbols are experimental data; full curves are best fits; numbers are triacetin mole fractions.



**Figure 2.** Experimental isopleths of the system  $\text{CO}_2$  + tributyrin: symbols are experimental data; full curves are best fits; numbers are tributyrin mole fractions



**Figure 3.** Experimental isopleths of the system  $\text{CO}_2$  + tricaproin: symbols are experimental data; full curves are best fits; numbers are tricaproin mole fractions;  $l_1l_2g$  three-phase equilibrium line.



**Figure 4.** Experimental isopleths of the system  $\text{CO}_2$  + tricaprylin: symbols are experimental data; full curves are best fits; numbers are tricaprylin mole fractions;  $l_1l_2g$  three-phase equilibrium line.

$l_2+l_1=g$ . Since no CO<sub>2</sub>-systems are known showing type-V fluid phase behavior in the classification of Van Konynenburg and Scott, these systems belong to type-III or type-IV. However, since type-IV is rarely met, it can be concluded that these systems show type-III fluid phase behavior.

## THERMODYNAMIC MODELING

In this work the capability of the GC-EoS equation of state (Skjold-Jørgensen, 1984) to predict the fluid phase behavior of mixtures of CO<sub>2</sub> with low-molecular weight triglycerides is studied. An upgraded version of the GC-EoS model has been successfully applied in previous work, to represent vapor-liquid (VLE), liquid-liquid (LLE) and vapor-liquid-liquid (VLLE) equilibria in mixtures of associating (Gros et al., 1996, 1997) and size-asymmetric mixtures (Bottini et al., 1999; Espinosa et al., 2000, 2002; Florusse et al., 2002).

The mixtures studied in this work can be represented by three main functional groups: paraffinic (CH<sub>2</sub> and CH<sub>3</sub>), triglyceride TG ((CH<sub>2</sub>COO)<sub>2</sub>CHCOO) and carbon dioxide (CO<sub>2</sub>). The values of the GC-EoS parameters for these functional groups have been reported by Espinosa et al. (2000).

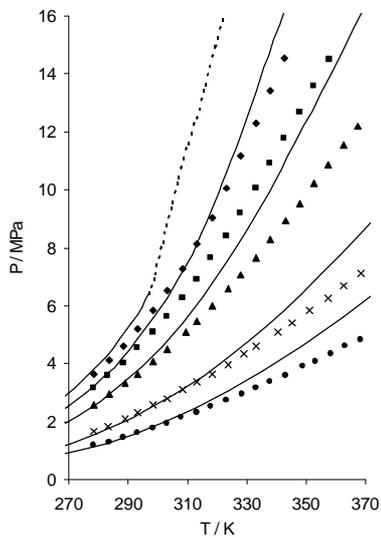
The free volume term in the GC-EoS equation is a function of the molecular size, represented by the critical hard-sphere diameter ( $d_c$ ). For high-volatile compounds, this parameter is determined from critical properties and vapor pressure data (Skjold-Jørgensen, 1984). This information is in general not available for high-molecular weight, low-volatile compounds and, therefore, an alternative procedure is required. Espinosa et al. (2002) proposed a correlation to calculate the  $d_c$  values of high molecular weight triglycerides and alkanes from the corresponding Van der Waals volumes. In this work, the critical hard sphere diameters of carbon dioxide ( $d_c = 3.130$ ) and triacetin ( $d_c = 5.617$ ) were determined from vapor pressure data, and those of tributyrin ( $d_c = 7.143$ ), tricaproin ( $d_c = 8.085$ ) and tricaprylin ( $d_c = 8.893$ ) were calculated from the correlation of Espinosa et al. (2002).

Figures 5 to 8 show the GC-EoS phase equilibrium predictions for the four binary systems studied in this work. Predictions are very good for the tricaproin and tricaprylin binaries, are quite good for tributyrin and deteriorate for triacetin.

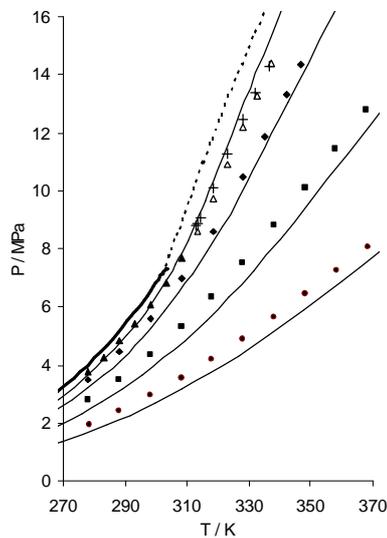
Triacetin behaves quite differently compared to the longer-chain triglycerides. For example, while these latter compounds are completely soluble in hexane, mixtures of triacetin and hexane are partly miscible at room temperature and pressure. At 350K, infinite dilution activity coefficients of hexane in triglycerides drop from 7.4 in triacetin (Bermudez et al., 2000) to 0.58 in tripalmitin (Foco et al., 1996). It becomes apparent from this behavior that there is a strongly interacting triglyceride backbone in these compounds, which is bare and free to interact in the short-chain triacetin molecules, but which is shielded by the long hydrocarbon chains in the higher molecular weight triglycerides.

It is clear from Figures 5 to 8 that, whilst the GC-EoS equation is able to give a good representation of the solubilities of CO<sub>2</sub> in tributyrin, tricaproin and tricaprylin, for CO<sub>2</sub> + triacetin the model predicts higher bubble pressures (i.e., lower CO<sub>2</sub> solubilities) than the experimental data. This means that stronger attractive CO<sub>2</sub>-TG interactions would be required to represent the experimental evidence.

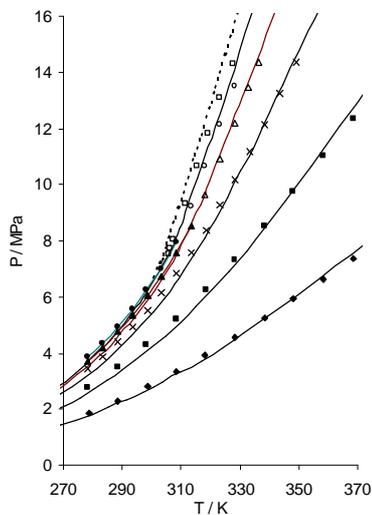
Taking into account the different behavior shown by triacetin and the results from the GC-EoS predictions, it was decided to represent the first member of the triglyceride family with its own molecular structure. The parameters for this new triacetin (AAA) molecular group were determined by fitting CO<sub>2</sub> + triacetin experimental data obtained in this work. Table 1 reports the parameters for the new AAA group, together with the



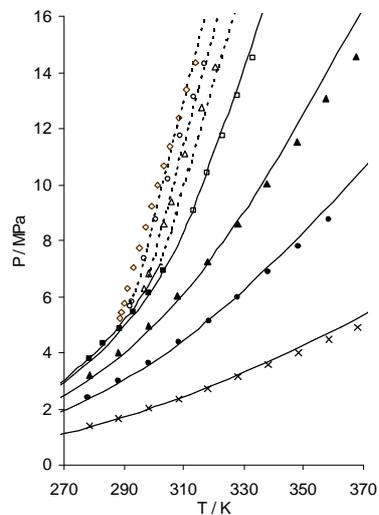
**Figure 5:** CO<sub>2</sub> + Triacetin system.  
 Exp. VLE: ● 0.6007; x 0.5037; ? 0.3058;  
 † 0.1974; ? 0.0998.  
 GC-EOS predictions: — VLE; - - - LLE.



**Figure 6:** CO<sub>2</sub> + Tributyrin system  
 Exp. VLE: ● 0.399; † 0.25; ? 0.13; ? 0.064  
 Exp. LLE: ? 0.064; + 0.015  
 GC-EOS predictions: — VLE; - - - - LLE



**Figure 7:** CO<sub>2</sub> + Tricaproin system.  
 Exp. VLE: ? 0.399; † 0.248; x 0.149;  
 ? 0.100; ● 0.073  
 Exp. LLE: ? 0.100; ? 0.073; ? 0.050  
 GC-EOS predictions: — VLE; - - - - LLE



**Figure 8:** CO<sub>2</sub> + Tricaprylin system  
 Exp. VLE: 0.497; ? 0.302; ? 0.197; † 0.105  
 Exp. LLE: ? 0.105; ? 0.075; ? 0.056; ? 0.037  
 GC-EOS predictions: — VLE; - - - - LLE

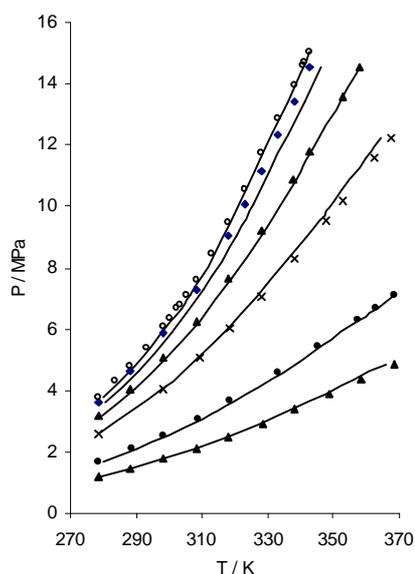
parameters of the original TG functional group, which remains the characteristic functional group for the other members of the triglyceride family. The table includes the values of the reference temperature ( $T^*$ ), the number of surface segments per mole ( $q$ ), the attractive energy interaction per segment ( $g$ ), the binary interaction parameter ( $k_{ij}$ ) and the non-randomness parameters ( $\alpha_{ij}$ ). Figure 9 shows the correlation of the experimental data obtained with the new AAA molecular group.

As it was already mentioned, a three-phase liquid-liquid-vapor ( $l_1l_2g$ ) locus was experimentally determined in the binaries  $\text{CO}_2 + \text{tricaproin}$  and  $\text{CO}_2 + \text{tricaprylin}$ . Figure 10 compares the experimental  $l_1l_2g$  locus with predictions by the GC-EoS equation. The agreement between experimental data and predictions is quite good.

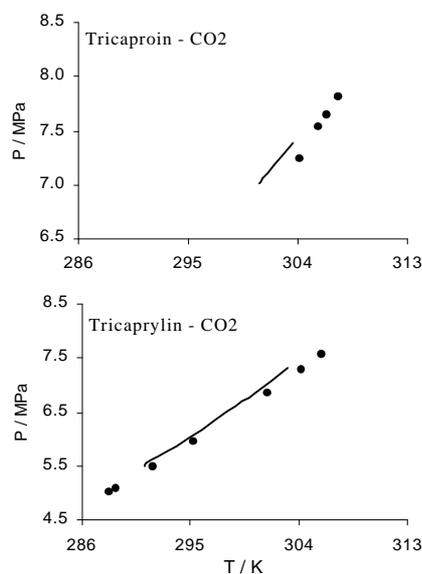
**Table 1:** GC-EoS parameters for the triglyceride (TG) and triacetin (AAA) groups

Group	$T^*$ (K)	$q$	$g^*$	$g'$	$g''$
<i>Pure group parameters</i> <sup>(†)</sup>					
TG	600	3.948	346350	-1.3460	0.0000
AAA	600	6.492	343331	-1.0270	0.0000
<i>Binary interaction parameters</i> <sup>(‡)</sup>					
Group I	Group j	$k_{ij}^*$	$k'_{ij}$	$a_{ij}$	$a_{ji}$
TG	$\text{CO}_2$	1.094	0.112	-1.651	-1.651
AAA	$\text{CO}_2$	1.1896	-0.0203	-17.498	-17.498

<sup>(†)</sup>  $g = g^*[1 + g' (T/T^*-1) + g'' \ln(T/T^*)]$     <sup>(‡)</sup>  $k_{ij} = k_{ij}^*[1 + k'_{ij} \ln(T/T_{ij}^*)]$



**Figure 9:**  $\text{CO}_2 + \text{Triacetin}$  system. Symbols: Experimental data; lines: GC-EoS predictions with parameters for the molecular AAA group.



**Figure 10:** Liquid-liquid-vapor locus for the  $\text{CO}_2 + \text{tricaproin}$  and  $\text{CO}_2 + \text{tricaprylin}$  systems. Symbols: experimental data; lines: GC-EoS predictions.

## CONCLUSIONS

Phase equilibrium measurements have been carried out for binary mixtures of CO<sub>2</sub> and a series of saturated triglycerides with increasing molecular weight. A liquid-liquid phase split was observed in mixtures of CO<sub>2</sub> with tributyrin, tricaproin and tricaprylin, while the three-phase equilibrium l<sub>1</sub>l<sub>2</sub>g in these systems have a critical end point of the nature l<sub>2</sub>+l<sub>1</sub>=g. It is believed that these systems belong to Type-III fluid phase behavior in the classification of Van Konynenburg and Scott.

The GC-EoS group contribution equation of state was applied to predict the fluid phase behavior of these mixtures. Good predictions of vapor-liquid, liquid-liquid and vapor-liquid-liquid equilibria in mixtures of CO<sub>2</sub> with tributyrin, tricaproin and tricaprylin were achieved, using a single set of group interaction parameters. A special molecular group (AAA) was defined to represent triacetin, the first member of the triglyceride family. This definition allowed a good representation of the experimental CO<sub>2</sub> + triacetin fluid phase behavior.

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