Liquid−Liquid−Supercritical Fluid Equilibria for Systems Containing Carbon Dioxide, Propane, and Triglycerides

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The use of mixed near-critical solvents such as CO_2 + propane, for vegetable oil extraction processes, has the advantage of the good solvent capacity of propane together with a nonflammable vapor phase due to the CO_2 content. The modeling of phase equilibria of these near-critical solvents with triglycerides using the GC-EOS model has been studied in several works; however, this model is not able to predict correctly the liquid−liquid−vapor region for mixtures of carbon dioxide and propane with triglycerides using the available group binary interaction parameters. In this work, new experimental phase equilibria data on the binary and ternary systems including CO_2, propane, and triacetin are presented. These data are useful to properly assess 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 addition of CO_2 increases liquid immiscibility.

Introduction

The use of CO_2 + propane solvent mixtures to extract oils from ground seeds is attractive from the standpoint of solvent power, selectivity, and safety. Liquid or supercritical carbon dioxide is immiscible with vegetable oils and has very low solvent power for the extraction of fixed oils. In contrast, propane at high pressure has complete miscibility with oils. Hegel et al.[1] proved the feasibility of extracting oil with the mixed solvent, which results in complete miscibility with the oil phase and possesses a nonflammable gas phase. In order to find the operating region the authors measured not only the three-phase equilibrium region (LLV) of the ternary CO_2 + propane + sunflower oil but also the bubble pressure of the binary CO_2 + sunflower oil.[2] The selection of optimum extraction conditions requires the phase equilibrium modeling of these mixtures under LLV and VLE equilibria.

Vegetable oils are complex mixtures of triglycerides (TAGs), which have hydrocarbon chains of different length and degree of unsaturation. However, their molecular structure can be characterized by a few functional groups. This feature supports the selection of a group contribution procedure to predict and correlate phase equilibria in mixtures with natural oils. The group contribution equation of state (GC-EoS[3]) proved to be an adequate model for size-asymmetric mixtures. It combines three well-known equations in phase equilibrium thermodynamics: the van der Waals equation of state, the Carnahan−Starling expression for hard spheres, and the NRTL equation. The mixing rule for the attractive part is a group contribution version of a density-dependent NRTL-type expression. Details of model equations can be found elsewhere.[3]

GC-EoS has shown good capabilities to model near-critical solvents with triglycerides.[4,5] However, the model predictions of the LLV region for mixtures of CO_2+ propane + triglycerides, using the available group energy binary parameters, were inaccurate. On the other hand, Florousse et al.[6] studied the modeling of phase equilibria of carbon dioxide with a series of triglycerides using the GC-EOS model. The authors reported that they could not represent the behavior of carbon dioxide with triacetin (the smallest triglyceride) with the same set of parameters used for the larger triglycerides.

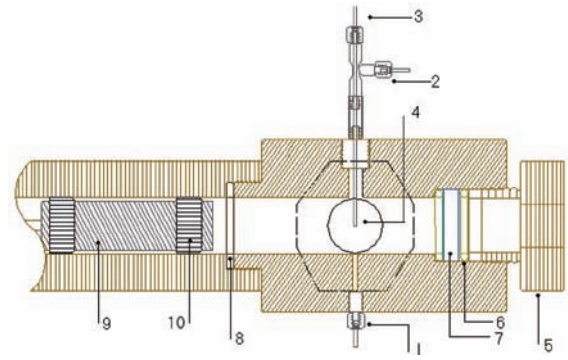

Figure 1. Variable-volume equilibrium cell: 1, heavy liquid-phase sampler; 2, vapor-phase sampler; 3, light liquid-phase sampler; 4, line of liquid-phase sampler; 5, view support; 6, O-ring seal; 7, view glass; 8, washer; 9, piston; 10, polypak seal.

This fact is pointing to the need of additional experimental information to revise the interaction between the main groups of the system under study. In this regard, it is also interesting to look at experimental infinite dilution activity coefficient (γ^{∞}) data of alkanes in triacetin. Bermudez et al.[7] reported the following values for hexane and heptane γ^{∞} in triacetin: 9.28 and 11.24, respectively. This means that alkanes form highly nonideal solutions in triacetin, and these binaries may exhibit LLE at room temperature.

In this work new experimental data on LLE of alkanes + triacetin, LLVE of CO_2 + propane + triacetin, and bubble pressures of CO_2 + triacetin and CO_2 + propane + sunflower oil are reported. All this information will be included in the parameter estimation of GC-EoS in order to better assess energy

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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	k_{ij}^*	k_{ij}'	α_{ij}	α_{ji}
AAA	CO_2	1.0000	0.0000	0.0000	0.0000
AAA	propane	0.905	0.0000	0.0000	0.0000

Table 3. Experimental Mutual Liquid Solubility for Hexane (1) + Triacetin (2) at 293 K

	hexane phase	triacetin phase
w_1	0.96 ± 0.005	0.05 ± 0.005
w_2	0.04 ± 0.005	0.95 ± 0.005

Table 4. Experimental Liquid−Liquid−Vapor-Phase Equilibria of the Triacetin (1) + Propane (2)

T/K	P/MPa	heavy liquid phase w_1 ± 0.030	light liquid phase w_1 ± 0.017	vapor phase w_1
308.1	1.15	0.92	0.06	*a*
323.1	1.70	0.91	0.07	*a*
333.1	2.14	0.89	0.08	*a*
342.6	2.60	0.87	*a*	*a*
353.2	3.10	0.78	*a*	*a*

[a] Not measured.

binary interaction parameters of the triglyceride group present in vegetable oils.

Materials and Methods

The materials and chemicals used in this work have the following purity: CO_2 99.7 %, propane 99 % (both gases were purchased to AGA S.A.). Triacetin has a minimum purity of 99 % (Fluka), hexane of chromatographic grade was purchsed from Sigma, and edible sunflower oil of commercial grade was purchased from Dow Agroscience, which has a high content of oleic acid (>87.75 %).

The mutual solubility data of triacetin + hexane at atmospheric pressure were obtained at 293.15 K 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 was determined. The temperature was measured by a platinum resistance sensor, and the estimated uncertainty was 0.2 K.

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 (Figure 1). The cell maximum volume, operating pressure, and temperature are 80 cm^3, 15 MPa, and 420 K, respectively.

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. The experimental procedure is as follows. The cell is evacuated and flushed with the solvent (CO_2 + propane) at low pressure to remove the residual air. A given amount of oil is weighted (between 10 and 20 g) and fed into the cell. The solvent is fed using a compressor and a manual pressure generator. Temperature was controlled inside the cell by a proportional controller and monitored with a platinum RTD probe. The pressure inside the cell was monitored with a pressure transducer (Ashcroft PT Indicator). Assuming the corresponding standard uncertainty had a normal distribution,

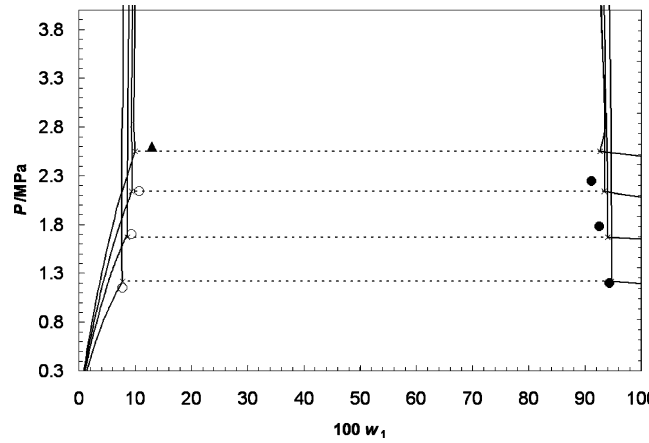

Figure 2. Propane + triacetin phase equilibria. Liquid−liquid−vapor equilibria. Lines, GC-EOS model correlation. ○, Experimental L_1 phase composition: variable volume equilibrium cell. ▲, Experimental L_1: Fixed volume equilibrium cell. ●, Experimental L_2 phase composition.

Table 5. Experimental Liquid−Vapor-Phase Equilibria: Bubble Points of the Mixture CO_2 (1) + Triacetin (2); Estimated Uncertainty of w_2 ± 0.015

w_2 = 0.28		w_2 = 0.55		w_2 = 0.65		w_2 = 0.78	
T/K	P/MPa	T/K	P/Mpa	T/K	P/Mpa	T/K	P/MPa
293.5	5.40	293.1	4.61	293.1	3.97		
298.1	6.14	298.1	5.21	300.1	4.95	298.2	3.38
308.1	7.87	308.1	6.49	308.1	5.71	308.2	4.28
313.1	8.85	313.1	7.30	313.2	6.41	313.2	4.74
		323.0	8.95	323.0	7.67	323.0	5.75

each expanded uncertainty was estimated to be 0.2 K in temperature and 0.05 MPa in pressure. After checking cell sealing under high pressure, the performance of the cell and pressure/temperature measurement instruments were calibrated with measurements of pure propane vapor pressure covering the temperature range of interest.

The experimental setup permits withdrawing samples from up to three phases (heavy liquid, light liquid, and vapor in this case). The concentration of triacetin in the heavy and light liquid phases was determined gravimetrically. Samples of the liquids and vapor phases were collected by depressurization and expansion into glass traps using manually operated valves (*Rheodyne*) with external loops. The total amount of the organic substance in the glass trap was about (0.1 to 1.1) g for the heavy liquid phase and about (0.008 to 0.06) g for the light liquid

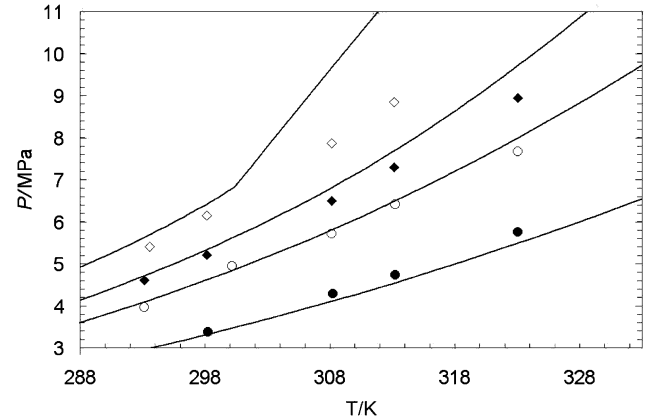

Figure 3. Bubble points of CO_2 (1) + triacetin (2). Lines, GC-EOS model predictions. ●, Experimental bubble points for w_2 = 0.777. ○, Experimental bubble points for w_2 = 0.649. ♦, Experimental bubble points for w_2 = 0.554. ◇, Experimental bubble points for w_2 = 0.277.

Table 6. Experimental L_1L_2V Equilibria for the System CO_2 (1) + Propane (2) + Triacetin (3)[a]

		L_1			L_2			V	
P/MPa	*T*/K	w_1	w_2	w_3	w_1	w_2	w_3	w_1	w_2
1.15	308.1	0.000	0.078	0.92	0.00	0.94	0.06	0.000	1.00
1.89	308.1	0.045	0.096	0.86	0.11	0.86	0.03	0.256	0.744
3.27	308.1	0.128	0.131	0.74	0.27	0.60	0.12	0.607	0.393
4.00	308.1	0.209	0.150	0.64				0.635	0.365
4.29	308.1	0.252	0.185	0.56	0.37	0.38	0.24	0.672	0.328
4.63	308.1	0.296	0.200	0.50	0.40	0.35	0.25	0.706	0.294
2.01	298.1	0.078	0.099	0.82	0.17	0.76	0.06	0.521	0.479
3.03	298.1	0.174	0.138	0.69	0.32	0.52	0.16	0.654	0.346
3.23	298.1	0.211	0.145	0.64				0.632	0.368
4.50	298.1	0.440	0.179	0.38				0.774	0.226

[a] Estimated uncertainty in L_1: $w_1 \pm 0.009$, $w_2 \pm 0.009$, $w_3 \pm 0.030$. Estimated uncertainty in L_2: $w_1 \pm 0.015$, $w_2 \pm 0.015$, $w_3 \pm 0.017$. Estimated uncertainty in V: $w_1 \pm 0.001$.

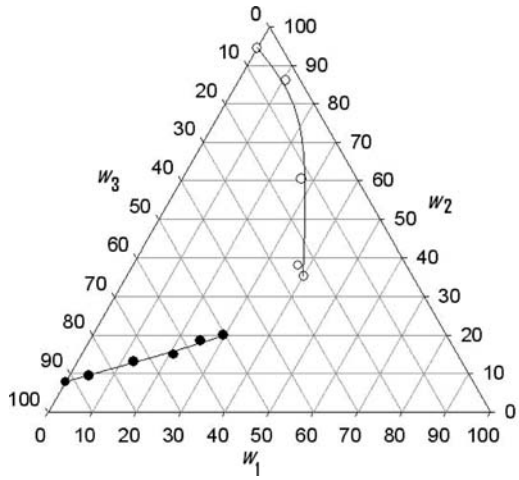

Figure 4. Liquid−liquid−vapor equilibria of the system CO_2 (1) + C_3 (2) + triacetin (3) at 308.15 K. Experimental behavior of the liquid phases with the operating pressure: ●, L_1 and ○, L_2. Data reported in Table 6.

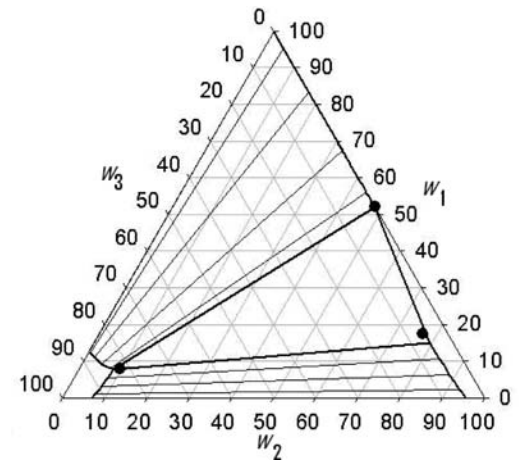

Figure 5. Liquid−liquid−vapor equilibria for the system CO_2 (1) + propane (2) + triacetin (3) at 298.15 K and 2.01 MPa. ●, Experimental liquid−liquid−vapor compositions. Solid lines, GC-EOS predictions of tie lines and binodal curve.

phase. The liquid samples were weighted in a precision balance with an accuracy of ± 0.0001 g. The amount of solvent (propane + carbon dioxide) in each phase was obtained volumetrically by expansion in a glass bottle of calibrated volume. In a typical experiment the measured volume of solvent was about 100 cm^3. The composition of the solvent (propane/CO_2) in each of the three phases was obtained by gas chromatography. Details of the experimental apparatus and technique are given by Hegel et al.[2]

The experiments of propane + triacetin were carried out over the LLVE line and also at VLE conditions in the temperature range of (308.15 to 353.15) K. In the ternary system CO_2 + propane + triacetin the lowest temperature was set at 298.15 K and the highest at 308.15 K. For the LLV equilibria measurements, in the heavy liquid phase the uncertainty of the triacetin mass fraction is ± 0.03, and for the solvents mass fraction the uncertainty is ± 0.009. In the light liquid phase the uncertainty of the triacetin mass fraction is ± 0.017 and for the solvents is ± 0.015. In the gas phase the uncertainty is ± 0.001. The uncertainties in composition were estimated by replication of experimental measurements under the same conditions. Above 333.15 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 liquid phase without having changes in the system pressure. The uncertainty in the pressure increases to 0.1 MPa at temperatures higher than 333.15 K.

Bubble pressures of the binary CO_2 + triacetin and the ternary CO_2 + propane + sunflower oil mixtures under conditions of complete liquid 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 ternary systems CO_2 + propane + sunflower oil was measured in the oil mass fraction range (0.20 to 0.44) and carbon dioxide mass fraction of (0.08 to 0.20). On the other hand, the bubble points for the binary system CO_2 + triacetin were measured in the range of carbon dioxide composition of (0.22 to 0.72) at temperatures between (293.15 and 323.15) K. The estimated uncertainty in the oil mass fraction in these measurements is ± 0.015.

Results and Discussion

When the GC-EOS model is applied to natural fatty oils, it is necessary to calculate the group composition of the oil from information on its fatty acid composition. In previous works,[4,5] the natural oil was represented by a single pseudotriacylglyceride with the following molecular structure: $[(CH_2COO)_2CHCOO]$-$(CH{=}CH)_m(CH_2)_n(CH_3)_3$. The term in square brackets represents the triglyceride functional group (TG). The values of *m* and *n* reproduce the molecular weight and degree of unsaturation of the natural oil and are calculated from the fatty acid composition of the oil. However, in this work, a new (molecular) group is defined $(CH_2COO)_2CHCOO)(CH3)_3$, called AAA. Therefore, the vegetable oil is represented here by a single pseudo-triglyceride with the following molecular structure: [AAA] $(CH_2)_{n-1}(CH_2{=}CH_2)_{m-1}$.

Table 7. Experimental Bubble Points of the System CO_2 (1) + Propane (2) + Sunflower Oil (3)

w_1	w_3	w_1	w_3	w_1	w_3	w_1	w_3
0.082	0.437	0.095	0.333	0.178	0.287	0.197	0.219
T/K	*P*/MPa	*T*/K	*P*/MPa	*T*/K	*P*/MPa	*T*/K	*P*/MPa
301.2	2.04	299.7	1.93	298.6	2.64	299.6	2.61
305.1	2.12	303.6	2.16	303.6	2.96	302.0	2.89
311.0	2.43	308.7	2.33	306.4	3.16	306.8	3.02
312.9	2.54	309.6	2.37	308.5	3.23	309.5	3.24
314.1	2.64	311.5	2.48	309.9	3.31[a]	310.2	3.33[a]
317.9	2.78	313.8	2.60				
319.9[a]	3.04[a]						

[a] LLV equilibria.

Table 1 shows the new molecular pure group parameters, and Table 2 shows the binary interaction parameters between AAA, propane, and CO_2. The other GC-EoS groups and interaction energy parameters used in this work are those of Espinosa et al.[5] More details on model equations and free volume contribution assessment can be found in the same manuscript.

Phase Behavior of Triacetin + Low Molecular Weight Alkanes. Table 3 reports the experimental results of liquid−liquid equilibria for the system triacetin + *n*-hexane at 293.15 K. The strong immiscibility of the binaries triacetin + alkanes is also observed in the experimental VLLE data of binary triacetin + propane reported in Table 4. Figure 2 shows the GC-EOS correlation for the system propane + triacetin along with the new experimental data. The system propane + triacetin shows liquid−liquid immiscibility up to the propane critical temperature. The liquid−liquid immiscibility below propane critical temperature will be observed up to very high pressures as predicted by the GC-EOS model. Therefore, the propane + triacetin binary is a type III system according to van Konynenburg and Scott[8] classification.

Bubble Pressure of Carbon Dioxide + Triacetin System. 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 given in Table 5 and shown in Figure 3 together with GC-EOS predictions. According to the GC-EOS predictions, the CO_2 + triacetin binary displays complete miscibility in the liquid phase for all mixtures with mass fractions lower than 60 % of CO_2. For higher concentrations of CO_2 the GC-EOS models predicts partial miscibility in the liquid phase; however, it has not been observed experimentally. This is quite a different behavior with respect to the CO_2 with long hydrocarbon chain triglycerides, like fats or vegetable oils, for which liquid-phase immiscibility persists over a certain composition range even at high pressures. It is clear that this information will be very valuable to obtain a more realistic parametrization of the group contribution equation of state thermodynamic model (GC-EOS).

Phase Behavior of Carbon Dioxide + Propane + Triacetin System. The LLV region of this system was studied at two different temperatures (298.15 and 308.15) K. The experimental results are given in Table 6. Figure 4 presents the behavior of the liquid phases in the LLV region together with GC-EoS predictions at 308.15 K, considering that for a ternary system, the LL tie lines in the LLV region are only a function of the operating pressure. In this case, the heterogeneous region decreases at constant temperature with the increase of carbon dioxide concentration, which is equivalent to higher pressures. Figure 5 shows the experimental LLV equilibria at 298.15 K and 2.10 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.

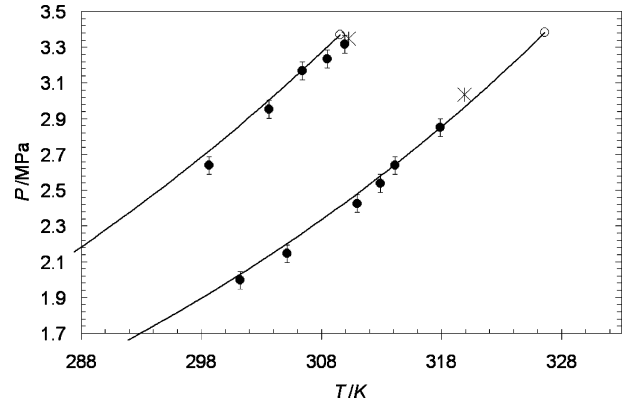

Figure 6. Bubble points of the system CO_2 (1) + propane (2) + sunflower oil (3). ●, Experimental liquid−vapor bubble point. *, Experimental liquid−liquid−vapor bubble point. −, GC-EOS liquid−vapor bubble point prediction. ○, GC-EOS liquid−liquid−vapor bubble point prediction.

Bubble Pressure of Carbon Dioxide + Propane + Sunflower Oil System. Bubble pressures of the ternary system CO_2 + propane + sunflower oil were measured from room temperature up to incipient liquid-phase split temperature at the bubble pressure condition. The experimental results are reported in Table 7. Figure 6 shows the bubble pressures for two isopleths. The composition of carbon dioxide has the strongest effect on the system vapor pressure. When the mass fraction of carbon dioxide goes from (8.3 to 18) % there is a clear difference in the temperature at which the liquid phase becomes heterogeneous. The bubble points prediction of the GC-EOS model agrees with the experimental phase equilibria, as can be observed in Figure 6. However, there is a disagreement in the prediction of the incipient appearance of liquid partial miscibility at high sunflower oil content.

Conclusions

New experimental information on the phase behavior of mixed supercritical solvents (CO_2 + propane) with the family of low and high molecular weight triglycerides is reported in this work. In previous studies[2] on carbon dioxide + propane + high molecular weight triglycerides, carbon dioxide played the role of an antisolvent, leading to liquid-phase split of the solvent mixture with the triglyceride at high carbon dioxide concentrations. In contrast, in the case of mixtures with triacetin, the carbon dioxide and propane solvent behavior are reversed. Carbon dioxide is completely miscible with triacetin, but triacetin is only slightly miscible with propane. Therefore, in a ternary system propane plays the role of an antisolvent.

The new experimental information is required to fit binary interaction parameters of a group contribution thermodynamic model. With the parameters determined in this work, GC-EoS is able to predict phase equilibria over a wide range of molecular weight triglycerides in mixtures with carbon dioxide and propane.

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