Phase behavior of carbon dioxide—low-molecular weight triglycerides binary systems: measurements and thermodynamic modeling

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Abstract

This contribution reports new experimental data on the fluid phase behavior of binary mixtures of carbon dioxide and three saturated, low-molecular weight triglycerides: 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 and 368 K and pressures up to 15 MPa. All mixtures show liquid–liquid immiscibility near the critical point of pure carbon dioxide. From the analysis of the experimental data, it became apparent that the CO_2-systems with tricaproin and tricaprylin have both type-IV fluid phase behavior in the classification of Van Konynenburg and Scott. 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.
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1. Introduction

Processing of natural products with supercritical fluid technology has been an extensive area of research during the past two decades. Examples of applications include extraction and refining, removal of contaminants, recovery of value-added products, etc. Vegetable oils are valuable natural products, consisting mainly of triglycerides, with a low fraction of diglycerides, free fatty acids and a number of minor components (sterols, tocopherols, phospholipids, etc.) that have added value as pharmaceuticals and food additives.

Supercritical fluids (SCF) are 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 [1–3]. Supercritical carbon dioxide, which is both nonflammable

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and nontoxic, is considered to be a substitute for hexane, the traditional solvent for liquid extraction [4].

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 [5,6]. 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 [4].

The design of these processes requires a good understanding of the phase behavior of systems having high-molecular weight compounds and low-molecular weight solvents. In particular, knowledge of the phase behavior of relevant triglyceride + SCF systems is a prerequisite in order to be able to select adequate process conditions. Not only experimental measurements on these systems provide quantitative insight into their general phase behavior, but in addition, important information can be distilled from 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 (tributyrin, tricaproin and tricaprylin) was investigated. Tributyrin molecules have three propyl groups attached to the triglyceride backbone. In the remaining triglycerides, the length of each aliphatic chain increases with two CH_2 groups; i.e., in comparison with tributyrin, there are six extra CH_2 groups in tricaproin and 12 in tricaprylin.

2. Experimental

Carbon dioxide (99.995 vol.%) was supplied by Hoek–Loos and was used without further purification. The supplier of all triglycerides was Fluka and the purity in all cases was better than 99 mol%. No further purification of the triglycerides was performed.

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. A sample of fixed known composition is confined

over mercury in the sealed end of a thick-walled Pyrex glass tube. The open end of the tube is placed in an autoclave, and immersed in mercury. Thus, mercury is used both, as a sealing and pressure transmitting fluid for the sample. The sample is stirred by means of a moving stainless steel ball, activated by reciprocating magnets. The autoclave is connected to a hydraulic oil system, generating the pressure by means of a screw type hand pump. The temperature of the sample is kept constant within ± 0.02 K, by circulating a thermostatic liquid through a glass thermostat

Table 1
Vapor–liquid and liquid–liquid isopleths of the system CO_2 (1) + tributyrin (2)

| T (K)	p (MPa)	T (K)	p (MPa)	T (K)	p (MPa)
Liquid–liquid equilibria					
$x_2 = 0.015$		$x_2 = 0.039$		$x_2 = 0.064$	
312.98	8.799	313.21	8.732	313.24	8.593
313.22	8.852	318.15	9.937	318.29	9.723
314.20	9.087	323.13	11.212	323.16	10.923
318.32	10.082	328.14	12.472	328.17	12.193
323.28	11.277	332.04	13.422	332.54	13.283
328.27	12.442	335.88	14.332	337.05	14.383
332.29	13.357				
336.54	14.282				
Vapor–liquid equilibria					
$x_2 = 0.015$		$x_2 = 0.039$		$x_2 = 0.064$	
278.31	3.917	278.40	3.842	278.27	3.753
283.31	4.437	283.23	4.332	283.19	4.243
288.19	4.992	288.26	4.892	288.29	4.808
293.41	5.642	293.30	5.512	293.28	5.408
298.21	6.302	298.22	6.172	298.33	6.083
303.17	7.037	303.17	6.907	303.24	6.813
303.24	7.047	304.17	7.067	308.31	7.653
304.25	7.212	305.29	7.252		
304.79	7.297	306.22	7.402		
305.20	7.362	308.17	7.742		
306.20	7.537				
308.26	7.882				
$x_2 = 0.130$		$x_2 = 0.250$		$x_2 = 0.399$	
278.23	3.481	278.31	2.781	278.50	1.926
288.40	4.456	288.42	3.516	288.28	2.396
298.43	5.611	298.42	4.361	298.26	2.931
308.27	6.956	308.19	5.291	308.27	3.531
318.35	8.596	318.22	6.361	318.14	4.176
328.22	10.461	328.11	7.526	328.24	4.886
335.20	11.886	338.10	8.781	338.24	5.636
342.21	13.336	348.12	10.101	348.38	6.421
347.02	14.336	358.08	11.441	358.52	7.231
		368.11	12.796	368.49	8.036
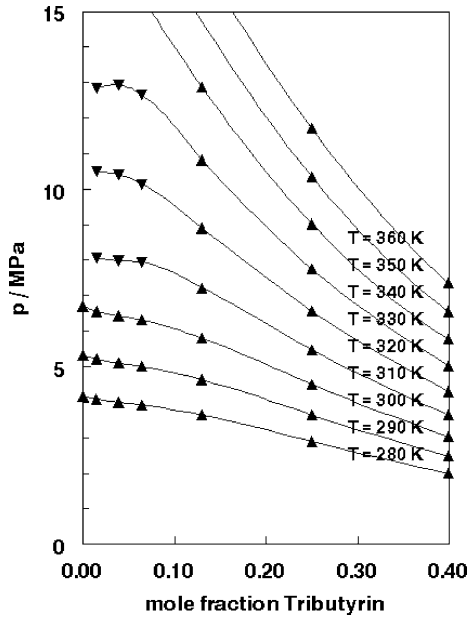
Fig. 1. The *p,x*-data of the system CO_2+tributyrin. (▲) lg-data and (▼) ll-data. All data points have been obtained from interpolation of the data collected in Table 1.
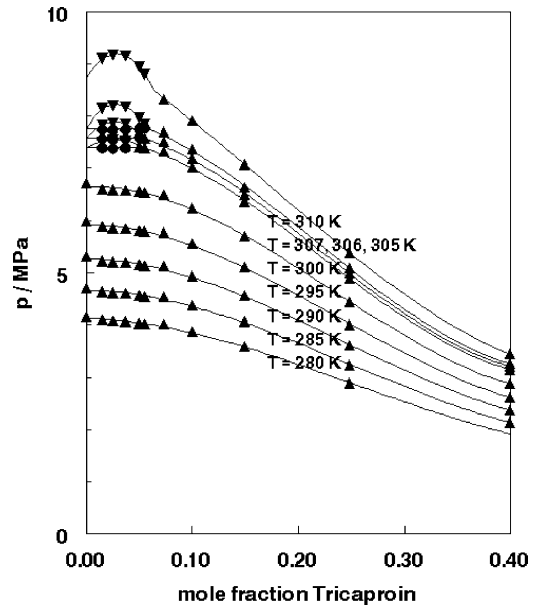

Fig. 2. The *p,x*-data of the system CO_2 + tricaproin. (▲) lg-data, (▼) ll-data, and (●) llg-data. All data points have been obtained from interpolation of the data collected in Tables 2 and 4.

jacket surrounding the glass tube. The temperature is measured with a platinum resistance thermometer (Pt-100) and the pressure with a dead weight pressure balance. Further details of the apparatus, experimental procedures, and accuracy of the measurements may be found elsewhere [7].

3. Experimental results

Tables 1–3 represent the primary vapor–liquid and liquid–liquid experimental data obtained for the binary systems of CO_2 and each one of the three triglycerides. The data are presented as isopleths, which is the way they have been obtained experimentally. From these data isothermal *p,x* sections can be derived straightforwardly (Figs. 1–3 for the three systems studied).

The system CO_2 + tricaprylin has also been studied by Bharath et al. [8] and Borch-Jensen and Mollerup [9]. Fig. 4 compares the experimental data obtained in this work with those from the literature, for the 313 and 353 K isotherms. There was a perfect match between our data and those of Borch-Jensen and Mollerup [9], but the data of Bharath et al. [8] are scattered.
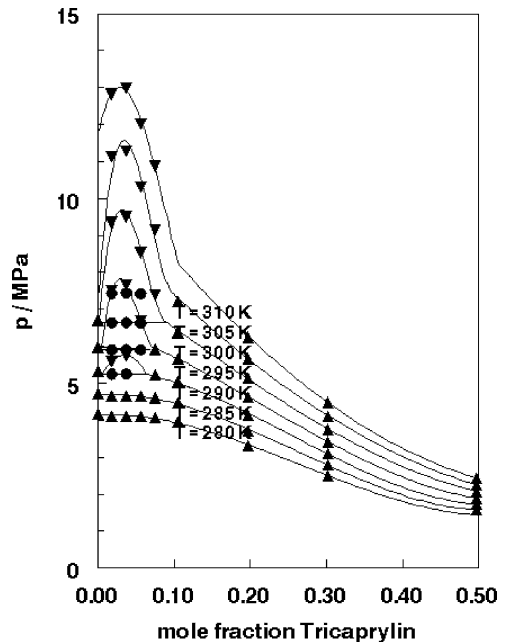

Fig. 3. The *p,x*-data of the system CO_2 + tricaprylin. (▲) lg-data, (▼) ll-data, and (●) llg-data. All data points have been obtained from interpolation of the data collected in Tables 3 and 5.

Table 2
Vapor–liquid and liquid–liquid isopleths of the system CO_2 (1) + tricaproin (2)

T (K)	p (MPa)	T (K)	p (MPa)	T (K)	p (MPa)	T (K)	p (MPa)
Liquid–liquid equilibria							
$x_2 = 0.015$		$x_2 = 0.025$		$x_2 = 0.037$		$x_2 = 0.050$	
304.43	7.324	304.17	7.263	304.32	7.293	305.68	7.543
304.72	7.414	304.67	7.428	304.41	7.323	306.22	7.718
307.33	8.249	305.29	7.638	308.15	8.553	307.17	8.028
311.25	9.489	307.47	8.358	313.19	10.178	311.21	9.338
315.16	10.689	312.85	10.068	318.09	11.698	315.27	10.633
319.11	11.864	318.33	11.758	323.09	13.188	319.17	11.833
323.14	13.024	322.39	12.958	327.00	14.318	323.26	13.063
327.31	14.184	326.41	14.123			327.42	14.283
$x_2 = 0.055$		$x_2 = 0.073$		$x_2 = 0.100$			
306.35	7.648	313.29	9.243	318.13	9.663		
306.63	7.728	318.09	10.638	323.06	10.898		
307.19	7.898	323.16	12.108	327.95	12.163		
308.10	8.193	328.04	13.498	332.91	13.438		
313.01	9.758			336.53	14.368		
317.96	11.303						
322.90	12.808						
327.79	14.223						
Vapor–liquid equilibria							
$x_2 = 0.015$		$x_2 = 0.025$		$x_2 = 0.037$		$x_2 = 0.050$	
278.43	3.939	278.38	3.913	278.39	3.903	278.25	3.853
283.39	4.459	283.56	4.453	283.30	4.413	283.32	4.373
288.40	5.029	288.27	4.993	288.30	4.983	288.25	4.938
293.26	5.644	293.35	5.633	293.37	5.623	293.34	5.583
298.26	6.339	298.30	6.323	298.26	6.308	298.36	6.293
303.25	7.104	303.29	7.103	303.25	7.098	303.18	7.078
304.26	7.269	304.05	7.238	304.21	7.263	304.24	7.263
						305.28	7.453
						305.40	7.478
						305.53	7.503
						305.59	7.513
$x_2 = 0.055$		$x_2 = 0.073$		$x_2 = 0.100$		$x_2 = 0.149$	
278.63	3.878	278.39	3.863	278.40	3.713	278.33	3.444
283.32	4.363	283.31	4.358	283.34	4.203	283.26	3.889
288.31	4.928	288.30	4.923	288.30	4.743	288.23	4.374
293.30	5.563	293.49	5.568	293.35	5.343	293.34	4.924
298.27	6.263	298.23	6.228	298.46	6.023	298.50	5.524
303.22	7.068	303.25	7.018	303.27	6.743	303.25	6.129
305.68	7.513	308.14	7.928	308.19	7.568	308.23	6.824
306.12	7.598			313.15	8.533	313.30	7.574
						318.23	8.379
						323.30	9.264
						328.23	10.184
						333.33	11.164
						338.20	12.144
						343.65	13.249
						349.19	14.344

Table 2 (*Continued*)

T (K)	p (MPa)	T (K)	p (MPa)	T (K)	p (MPa)	T (K)	p (MPa)
$x_2 = 0.248$		$x_2 = 0.399$					
278.33	2.776	278.50	1.858				
288.21	3.471	288.35	2.298				
298.23	4.281	298.35	2.793				
308.16	5.201	308.15	3.328				
308.24	5.206	318.14	3.933				
318.22	6.231	328.12	4.563				
328.18	7.336	338.12	5.223				
338.21	8.531	348.19	5.923				
348.17	9.766	358.21	6.633				
358.11	11.021	368.30	7.363				
368.29	12.331						

Table 3
Vapor–liquid and liquid–liquid isopleths of the system CO_2 (1) + tricaprylin (2)

T (K)	p (MPa)	T (K)	p (MPa)	T (K)	p (MPa)	T (K)	p (MPa)
Liquid–liquid equilibria							
$x_2 = 0.018$		$x_2 = 0.037$		$x_2 = 0.056$		$x_2 = 0.075$	
288.74	5.103	288.68	5.232	292.34	5.668	296.97	6.290
288.96	5.188	289.23	5.452	292.76	5.828	298.36	6.805
289.35	5.338	290.08	5.782	296.83	7.368	303.28	8.565
294.26	7.233	291.45	6.317	300.66	8.768	305.62	9.375
299.23	9.073	293.34	7.037	304.66	10.193	310.65	11.090
304.16	10.838	295.23	7.752	309.13	11.733	315.78	12.770
310.20	12.893	297.20	8.482	313.33	13.128	320.33	14.195
314.25	14.228	299.20	9.217	316.92	14.293		
		301.32	9.987				
		303.21	10.662				
		305.22	11.357				
		308.20	12.392				
		311.15	13.377				
		314.18	14.372				
$x_2 = 0.105$							
313.28	9.042						
318.15	10.417						
323.08	11.757						
328.23	13.172						
333.20	14.482						
Vapor–liquid equilibria							
$x_2 = 0.018$		$x_2 = 0.037$		$x_2 = 0.056$		$x_2 = 0.075$	
278.36	3.943	278.36	3.937	278.45	3.938	278.25	3.890
280.87	4.198	283.34	4.462	280.88	4.193	283.45	4.430
283.33	4.468	287.76	4.982	283.24	4.443	288.34	5.010
285.73	4.738	288.26	5.062	285.86	4.743	293.33	5.670
287.30	4.923			288.37	5.043	295.83	6.030
287.80	4.983			290.84	5.358		
288.07	5.018			291.27	5.418		
288.29	5.043			291.83	5.493		
288.40	5.058						
288.51	5.073						
288.60	5.083						

Table 3 (*Continued*)

T (K)	p (MPa)	T (K)	p (MPa)	T (K)	p (MPa)	T (K)	p (MPa)
$x_2 = 0.105$		$x_2 = 0.197$		$x_2 = 0.302$		$x_2 = 0.497$	
278.34	3.772	278.34	3.177	278.32	2.419	278.36	1.396
283.29	4.297	288.34	4.002	288.14	2.979	288.34	1.676
288.47	4.847	298.29	4.962	298.37	3.639	298.24	2.011
293.28	5.432	308.11	6.022	308.27	4.354	308.17	2.371
298.30	6.122	318.06	7.247	318.29	5.144	318.21	2.746
303.29	6.907	327.92	8.592	328.32	5.984	328.14	3.151
308.24	7.847	337.83	10.042	338.26	6.864	338.15	3.576
		347.78	11.542	348.30	7.784	348.09	4.011
		357.62	13.072	358.32	8.724	358.24	4.456
		367.43	14.557	368.30	9.659	368.19	4.916

A three-phase liquid–liquid–vapor (l_1l_2g) locus could be established in the CO_2 + tricaproin and CO_2 + tricaprylin binary systems, both with a critical endpoint of the nature $l_2 + l_1 = g$. The experimental liquid–liquid–vapor data are reported in Tables 4 and 5.

An interesting observation in the CO_2-systems with caproin and caprylin is their type of fluid phase behavior. From their p,x-diagrams (Figs. 2 and 3, respectively), it easily can be observed that in each system there is a critical locus of the nature $l_1 = l_2$. These

loci can be obtained by connecting the maxima of the two-phase domes $l_1 + l_2$. In a p,T-diagram, these loci run with a positive slope from higher to lower temperatures and pressures, and will intersect the three-phase equilibrium l_1l_2g. Consequently, this will result in the occurrence of a critical endpoint of the nature $l_1 = l_2 + g$. Since in both systems it was established experimentally that the three-phase equilibria end in a critical endpoint of the nature $l_2 + l_1 = g$, this easily may lead to the conclusion that both systems will have type-V (see Fig. 5e) fluid phase behavior. However, since in the literature, no binary CO_2-systems showing type-V fluid phase behavior [10] are known, the only conclusion that can be drawn is that these

Table 4
Liquid–liquid–vapor locus of the system CO_2 (1) + tricaproin (2)

T (K)	p (MPa)	T (K)	p (MPa)	T (K)	p (MPa)
$x_2 = 0.015$		$x_2 = 0.025$		$x_2 = 0.037$	
304.26	7.263	304.17	7.241	304.32	7.276
304.35	7.283	304.67	7.322	304.41	7.294
304.43	7.299	305.29	7.424	304.78	7.350
304.71	7.347	306.06	7.563	305.78	7.523
305.26	7.431	306.84	7.701	306.73	7.694
306.24	7.601	307.34	7.799	307.46	7.825[a]
307.14	7.763	307.37	7.809		
307.32	7.799	307.47	7.819[a]		
307.41	7.817				
307.44	7.821				
307.47	7.825[a]				
$x_2 = 0.050$		$x_2 = 0.055$			
305.68	7.533	306.35	7.644		
305.79	7.549	306.61	7.699		
306.22	7.623	307.19	7.791		
307.17	7.794	307.28	7.818[a]		
307.27	7.814				
307.30	7.819				

[a] UCEP.

Table 5
Liquid–liquid–vapor locus of the system CO_2 (1) + tricaprylin (2)

T (K)	p (MPa)	T (K)	p (MPa)	T (K)	p (MPa)
$x_2 = 0.018$		$x_2 = 0.037$		$x_2 = 0.056$	
288.74	5.097	288.25	5.037	291.83	5.485
288.96	5.121	288.40	5.060	292.34	5.550
289.35	5.169	288.68	5.088	292.76	5.604
294.26	5.801	289.23	5.159	296.83	6.159
299.23	6.519	290.08	5.262	300.66	6.726
304.16	7.299	291.45	5.434	304.66	7.365
305.33	7.485	293.34	5.687	305.65	7.529
305.38	7.495	295.24	5.942	305.72	7.543
305.47	7.515	297.20	6.223	305.77	7.552
305.51	7.521	299.19	6.520	305.82	7.561[a]
305.58	7.529	301.32	6.846		
305.63	7.537	303.22	7.152		
305.64	7.539[a]	305.22	7.488		
		305.55	7.538[a]		

[a] UCEP.
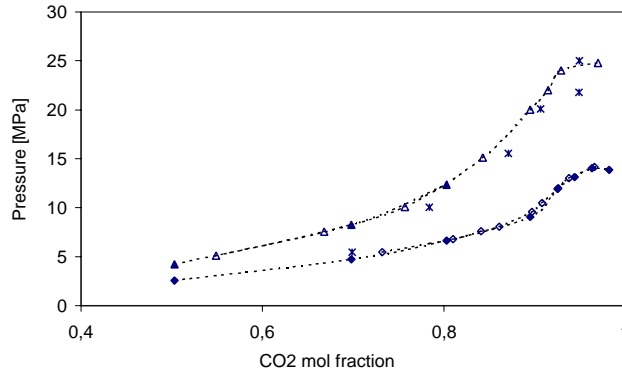
Fig. 4. Comparison of data for the system CO_2 + tricaprylin. $T = 313$ K: (◆) this work; (◇) [9]; $T = 333$ K: (▲) this work (△) [9]; (✕) [8]. The dashed/dotted lines connect the data obtained in this work and those of [9].
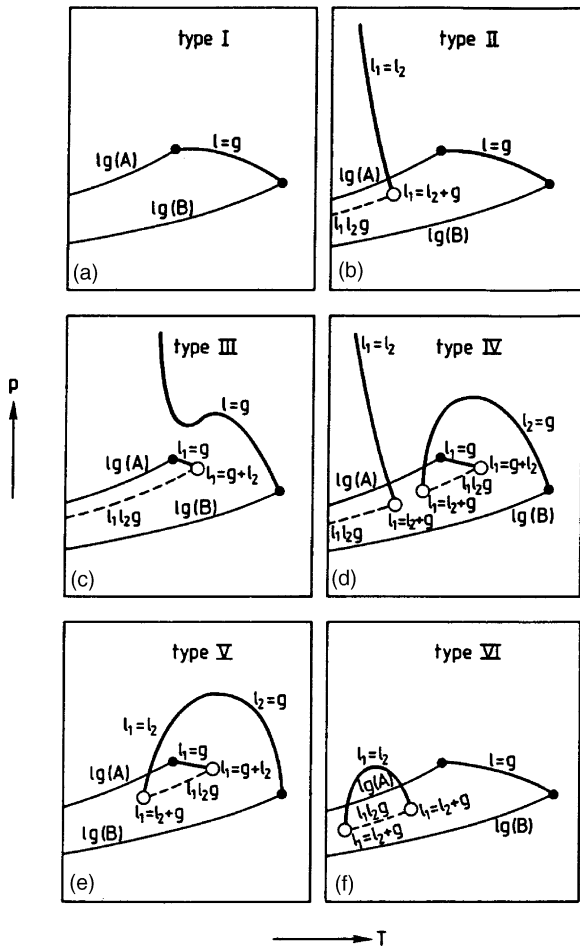

Fig. 5. Classification of fluid phase equilibria according to Van Konynenburg and Scott.

systems must have type-IV fluid phase behavior (see Fig. 5d). Unfortunately, the low-temperature part of the three-phase equilibrium l_1l_2g (see Fig. 5d) has not been observed experimentally. However, it could be located at such low temperatures that it is hidden by the occurrence of the solid phase of the triglycerides.
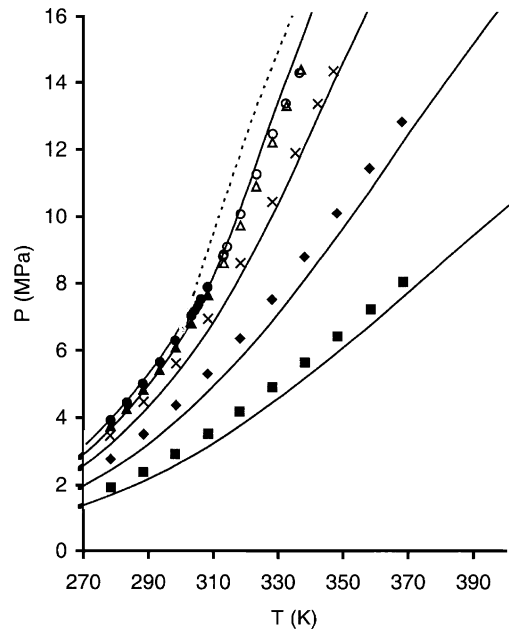
Fig. 6. CO_2 + tributyrin system. Exp. VLE: Tributyrin mol fractions: (●) 0.015; (▲) 0.064; (×) 0.13; (◆) 0.25; (■) 0.399; Exp. LLE: tributyrin mol fractions: (○) 0.015; (△) 0.064; GC–EOS predictions: (—) VLE; (- - -) LLE.

4. Thermodynamic modeling

In this work the capability of the group contribution equation of state (GC–EoS) [11] to predict the fluid phase behavior of mixtures of CO_2 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 [12,13] and size-asymmetric mixtures [14–17].

The mixtures studied in this work can be represented by three main functional groups: paraffinic (CH_2 and CH_3), triglyceride TG (($CH_2COO)_2CHCOO$) and carbon dioxide (CO_2). The values of the GC–EoS parameters for these functional groups have been reported previously by Espinosa et al. [15].

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 [11]. This information is in general not available for high-molecular weight, low-volatile compounds and, therefore, an alternative procedure is required. Espinosa et al. [16] 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 diameter of carbon dioxide ($d_c = 3.130$) was 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. [16].

Figs. 6–8 show the GC–EoS phase equilibrium predictions for the three binary systems studied in this work. Predictions were in very good agreement with the experimental results for the tricaproin and tricaprylin binary systems, and in good agreement for the tributyrin system.
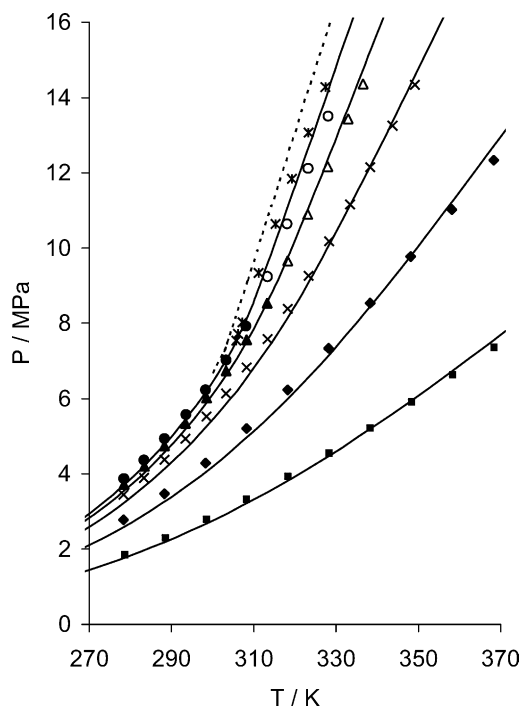

Fig. 7. CO_2 + tricaproin system. Exp. VLE: Tricaproin mol fractions: (●) 0.073; (▲) 0.100; (×) 0.149; (◆) 0.248; (■) 0.399; Exp. LLE: Tricaproin mol fractions: (✳) 0.05; (○) 0.073; (△) 0.100; GC–EOS predictions: (——) VLE; (- - -) LLE.
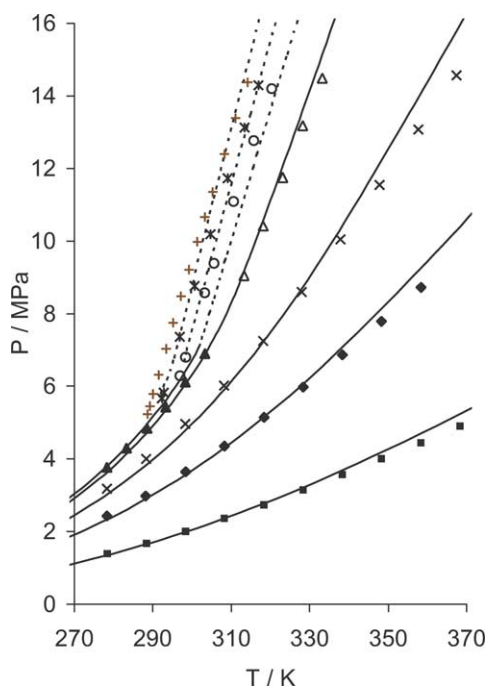

Fig. 8. CO_2 + tricaprylin system Exp. VLE: tricaprylin mol fractions: (▲) 0.105; (×) 0.197; (◆) 0.302; (■) 0.497; Exp. LLE: tricaprylin mol fractions: (+) 0.037; (✳) 0.056; (○) 0.075; (△) 0.105; GC–EOS predictions: (——) VLE; (- - -) LLE.
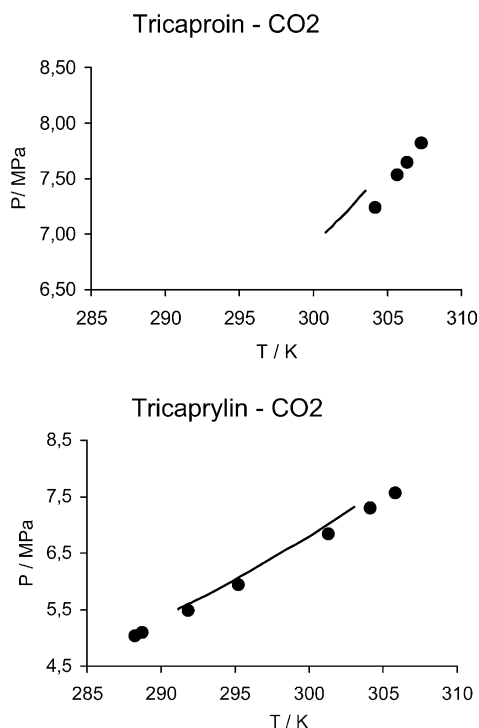
Fig. 9. Liquid–liquid–vapor locus for the CO_2 + tricaproin and CO_2 + tricaprylin systems. Symbols: experimental data; lines: GC–EoS predictions.

As mentioned before, a three-phase liquid–liquid–vapor ($l_1 l_2 g$) locus was experimentally determined in the binary systems CO_2 + tricaproin and CO_2 + tricaprylin. Fig. 9 compares the experimental $l_1 l_2 g$ locus with predictions by the GC–EoS equation. The agreement between experimental data and predictions was good.

5. Conclusions

Phase equilibrium measurements have been carried out for binary mixtures of CO_2 and a series of saturated triglycerides with increasing molecular weight. A liquid–liquid phase split was observed in mixtures of CO_2 with tributyrin, tricaproin and tricaprylin, while the three-phase equilibrium $l_1 l_2 g$ in these systems have a critical end point of the nature $l_2 + l_1 = g$. From the analysis of the experimental data, it could be concluded that the systems with tricaproin and tricaprylin

both show type-IV fluid phase behavior in the classification of Van Konynenburg and Scott. The experimental information of the system with tributyrin is too limited to establish its type of fluid phase behavior. However, type-IV for this system also seems to be most likely. 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 were achieved, using a single set of group interaction parameters.

References

[1] R. Eggers, U. Sievers, W. Stein, High-pressure extraction of oil seeds, J. Am. Oil. Chem. Soc. 62 (8) (1985) 1222.
[2] J.P. Friedrich, G.R. List, A.J. Heakin, Petroleum-free extraction of oil from soybeans with supercritical CO_2, J. Am. Oil. Chem. Soc 59 (7) (1982) 288.
[3] A.K. Klee, N.B. Bulley, M. Fattori, A. Miesen, Modeling of supercritical carbon dioxide extraction of canola oliseed in fixed beds, J. Am. Oil. Chem. Soc. 63 (7) (1986) 921.
[4] T. Bamberger, J.C. Erickson, C.L. Cooney, S.K. Kumar, Measurement and model prediction of solubilities of pure fatty acids, pure triglycerides and mixtures of triglycerides in supercritical carbon dioxide, J. Chem. Eng. Data 33 (1988) 327.
[5] H. Passino, The Solexol process, Ind. Eng. Chem. 41 (1949) 280.
[6] N. Dickinson, J. Meyers, Solexol fractionation of menhaden oil, J. Am. Oil Chem. Soc. 29 (1952) 235.
[7] S. Raeissi, C.J. Peters, Bubble-point pressures of the binary system carbon dioxide + linalool, J. Supercritical Fluids 20 (2001) 221.
[8] R. Bharath, S. Yamane, H. Inomata, T. Adschiri, K. Arai, Phase equilibria of supercritical CO_2: fatty oil component binary systems, Fluid Phase Equilib. 83 (1993) 183–192.
[9] C. Borch-Jensen, J. Mollerup, Phase equilibria of carbon dioxide and tricaprylin, J. Supercrit. Fluids 10 (1997) 87–93.
[10] C.J. Peters, K. Gauter, The occurrence of holes in ternary fluid multiphase mixtures systems of near-critical carbon dioxide and certain solutes, Chem. Rev. 99 (1999) 419–431.
[11] S. Skjold-Jørgensen, Gas solubility calculations II. Application of a new group-contribution equation of state, Fluid Phase Equilib. 16 (1984) 317–351.

[12] H. Gros, S.B. Bottini, E.A. Brignole, A group contribution equation of state for associating mixtures, Fluid Phase Equilib. 116 (1996) 537.

[13] H. Gross, S.B. Bottini, E.A. Brignole, High pressure phase equilibrium modeling of mixtures containing associating compounds and gases, Fluid Phase Equilib. 139 (1997) 75.

[14] S.B. Bottini, T. Fornari, E.A. Brignole, Phase equilibrium modeling of triglycerides with near critical solvents, Fluid Phase Equilib. 158–160 (1999) 211.

[15] S. Espinosa, G.M. Foco, A. Bermudez, T. Fornari, Revision and extension of the group contribution equation of state to new solvent groups and higher molecular weight alkanes, Fluid Phase Equilib. 172 (2000) 129.

[16] S. Espinosa, T. Fornari, S.B. Bottini, E.A. Brignole, Phase equilibria in mixtures of fatty oils and derivatives with near critical fluids using the GC–EoS model, J. Supercrit. Fluids 23 (2002) 91.

[17] L.J. Florusse, T. Fornari, S.B. Bottini, C.J. Peters, Phase behavior of the binary system near-critical dimethylether and tripalmitin: measurements and thermodynamic modeling, J. Supercrit. Fluids 22 (2002) 1.