J Am Oil Chem Soc (2011) 88:1263–1269
DOI 10.1007/s11746-011-1786-z

ORIGINAL PAPER

Phase Equilibrium Measurements of Sacha Inchi Oil (*Plukenetia volubilis*) and CO_2 at High Pressures

Ivor M. do Prado · Willyan M. Giufrida · Víctor H. Alvarez · Vladimir F. Cabral · Sócrates Quispe-Condori · Marleny D. A. Saldaña · Lucio Cardozo-Filho

Received: 18 November 2010 / Revised: 11 February 2011 / Accepted: 14 February 2011 / Published online: 5 March 2011

Abstract New data on phase equilibria for Sacha inchi seed oil in carbon dioxide have been measured using a variable volume cell phase equilibria system at temperatures of 303, 313 and 323 K and at pressures ranging from 4.3 to 27.7 MPa. The CO_2 mole fraction varied from 0.7488 to 0.9997. At the studied concentrations, phase transitions of vapor-liquid, liquid-liquid-vapor and liquid-liquid were observed. Sacha inchi oil contains 47% of omega-3 fatty acids, with a ratio of 0.76:1 for omega-6:omega-3, which is good for human health. The Peng-Robinson equation of state was used to describe the experimental data. A qualitative agreement was obtained between experimental and calculated data for the binary system CO_2 and Sacha inchi seed oil.

Keywords Carbon dioxide · Equation of state · High pressure · Omega-3 · Phase equilibria · *Plukenetia volubilis* · Sacha inchi seed oil

Introduction

The addition of polyunsaturated fatty acids (PUFA) to functional food ingredients and their consumption in dietary supplements have experienced significant increases [1]. PUFA have been associated with a variety of health benefits such as decrease risk of cardiovascular disease and prevent complications of lipotoxicity [2]. Fish and flax oils are the commonly sources of PUFA [3]. Recently, seeds of Sacha inchi (*Plukenetia volubilis*) from a Peruvian tree have been commercialized as an alternative source of PUFA due to its high oil (35–60%) and protein (27–33%) contents [4]. Sacha inchi is a millenarian legacy of the Inca civilization that has been cultivated to date by the native communities of the Peruvian Amazon. Sacha inchi seed oil is an excellent source of PUFA, composed mainly by linolenic (C18:3 ω -3) and linoleic (C18:2 ω-6) acids [4]. However, one of the major drawbacks of oils containing a high amount of PUFA is their low stability and rapid oxidation, which involves the formation of toxic products such as peroxides or undesirable off-flavor compounds [5].

Commercially, unrefined Sacha inchi seed oil is produced by cold pressing. Although this process preserves its original composition such as PUFA content, the yield is low (38.4%) compared to Soxhlet extraction (54.3%). But, Soxhlet extraction uses high temperatures that reduce the quantity of PUFA in the oil due to oxidation by high temperature exposure [5, 6]. Therefore, supercritical fluid (SCF) extraction is another alternative process for the extraction of oils [7]. This extraction method exploits the high solvation power, low viscosity, and high diffusion coefficient offered by the supercritical fluid to increase the extraction yield.

Phase equilibrium measurements of soybean or castor oil + supercritical CO_2 and fish oil + supercritical CO_2 have been reported earlier by Ndiaye et al. [8] and Riha and Brunner [9], respectively. These authors report only pressure transitions and the correlation of their data with equations of state (EoS). There is great interest in thermodynamic models that are able to correlate and predict

I. M. do Prado · V. H. Alvarez · S. Quispe-Condori · M. D. A. Saldaña (✉)
Department of Agricultural, Food and Nutritional Science, University of Alberta, Edmonton, AB T6G 2P5, Canada
e-mail: marleny@ualberta.ca

W. M. Giufrida · V. F. Cabral · L. Cardozo-Filho
Department of Chemical Engineering, Universidade Estadual de Maringá, CEP 87020/900 Maringá, Paraná, Brazil

the phase behavior of oil systems in CO_2. These models are generally based on: (i) an equation of state approach like Peng-Robinson equation of state (PR-EoS) [10], (ii) a density-based approach, or (iii) a solubility parameter approach. Density-based correlations are also used to determine the solubility of a solute in a supercritical fluid, attempting to explain the common observation that the logarithm of the solubility is linearly dependent on the log of the SCF density. Chrastil equation is commonly used for this purpose. These approaches as well as others are discussed in detail by Brennecke and Eckert [11]. These approaches show that the solubility depends mainly on physicochemical properties of both the solvent and the solute. Some important properties include the density of the solvent and the solute and the vapor pressure of the solute as well as in some cases the critical properties and acentric factor.

Extraction of Sacha inchi seed oil has been reported using supercritical CO_2 [6]. The global extraction yield and oil solubility were determined at temperatures of 313, 323 and 333 K and pressures of 30 and 40 MPa. However, phase equilibria of Sacha inchi seed oil at high pressures have not been reported. Knowledge of phase equilibrium at high pressures is crucial in any process design such as SCF extraction [12], reaction and particle formation. Therefore, the objective of this study was to measure the phase equilibria for Sacha inchi seed oil in carbon dioxide at high pressures and to model the phase behavior using PR-EoS.

Material and Methods

Materials

Cold pressed and unrefined Sacha inchi seed oil was obtained from Industrias Amazonicas (Lima, Peru). Sodium methoxide solution 0.5 M in methanol, methyl acetate and methyl heptadecanoate were purchased from Fluka Sigma Aldrich Co. (St. Louis, MO, USA). Hexane was acquired from Fisher Scientific (Ottawa, ON, Canada). Carbon dioxide with purity >99.98 mol% was supplied by White Martins (Maringa, PR, Brazil).

Fatty Acid Composition

The fatty acid (FA) composition of Sacha inchi seed oil was determined using a modified fatty acid methyl esters (FAME) method. The FAME were analyzed using a gas chromatograph with a flame ionization detector (GC-FID) (Varian Model 3400, Agilent Technologies, Mississauga, ON, Canada) equipped with a fused silica capillary column (60 m × 0.32 mm, DB-5, J&W Scientific, Folsom, CA, USA). The carrier gas was helium. The temperatures of the injector and detector were 508 and 523 K, respectively. The column was heated to 343 K and held for 0.2 min, programmed to increase at a rate of 35 K/min to 483 K, then at a rate of 2 K/min to 508 K and held for 8.3 min.

Sacha inchi oil dissolved in hexane (100 μL) was transmethylated to FAME by heating at 323 K for 15 min with a mixture of 0.5 M sodium methoxide (80 μL) and methyl acetate (40 μL). In order to identify Sacha inchi FAME composition, methyl heptadecanoate was used as an internal standard at the concentration of 1 mg/mL as this compound was not present in Sacha inchi seed oil original composition. One milliliter of the standard solution was added to the mixture. To separate the FAME, 2 mL of water and 2 mL of hexane were added to the mixture and the solution was centrifuged (GLC-2B Sorvall Dupont Instruments, Wilmington, NC, USA) at $1237 \times g$ for 1 min. The supernatant was separated and 1 μL of the sample was injected to the gas chromatograph.

Phase Equilibrium Apparatus and Procedure

Phase equilibrium experiments (cloud point) for the system Sacha inchi seed oil + CO_2 were carried out using the static synthetic method in a high pressure variable-volume view cell. The experimental apparatus and procedure have been well described in previous studies [12–14]. The experimental unit consists of a 25 mL variable-volume view cell with two sapphire windows for visual observation, an absolute pressure transducer (Smar, model LD 301, Sertãozinho, SP, Brazil) with an uncertainty of ±0.03 MPa, a portable pressure data acquisition system (Smar, model HT 201, Sertãozinho, SP, Brazil), and a syringe pump (ISCO, model 260D, Lincoln, USA). The equilibrium cell contains a movable piston, which allows controlling the pressure inside the cell. Phase transitions were identified visually through the manipulation of pressure using the syringe pump and the CO_2 as the pneumatic fluid. Phase transitions were visually recorded as dew points. First, a known amount of Sacha inchi seed oil was loaded into the equilibrium cell with a syringe weighed on a precision scale balance (Marte, model AM220, Santa Rita do Sapucaí, MG, Brazil) with an uncertainty of ±0.001. The cell was then flushed with low pressure CO_2 to remove any residual air. The amount of CO_2 remaining in the equilibrium cell is negligible ($\sim 10^{-5}$ mol) when compared to the total amount of CO_2 used to determine the experimental data. A known amount of CO_2 was loaded using the syringe pump (with an uncertainty of ±0.005 g). Then, the mixture inside the cell was continuously agitated with a Teflon-coated magnetic stirring bar. After achieving the desired temperature, the pressure was increased until visualization of one-phase in the cell. The system was kept at this point for at least 30 min to allow stabilization. Then, the pressure was slowly decreased (at a rate of 0.1–0.3 MPa/min) until a new phase was observed. The experiments were carried out at 303, 313 and 323 K. All experiments were conducted in triplicate.

Thermodynamic Modeling of Experimental Data

The isofugacity approach based on the PR-EoS with the van der Waals quadratic mixing rule with two adjustable parameters, k_{ij} and l_{ij}, were used for the thermodynamic model. The classic van der Waals mixing and combining rules, with interaction parameters are:

$$a = \sum_{i=1}^{nc} \sum_{j=1}^{nc} x_i x_j \sqrt{a_i a_j}(1 - k_{ij}) \tag{1}$$

$$b = \sum_{i=1}^{nc} \sum_{j=1}^{nc} x_i x_j \left(\frac{b_i + b_j}{2}\right)(1 - l_{ij}) \tag{2}$$

where a and b are mixture EoS parameters, x_i is the mole fraction for component i, and nc is the number of components. The temperature-independent interaction parameters (k_{ij} and l_{ij}) were optimized using a genetic algorithm [15] applied to bubble point calculations for the three isotherms. The relative percent deviations in pressure were minimized using the following objective function (OF) [16]:

$$\mathrm{OF} = \sum_{i=1}^{N} \left|(P_i^{\mathrm{cal}} - P_i^{\mathrm{exp}})\right| / P_i^{\mathrm{exp}} \tag{3}$$

where P_i^{cal} is the calculated pressure, P_i^{exp} is the experimental pressure, and N is the number of experimental data points.

Results and Discussion

Fatty Acid Composition

The fatty acid composition of Sacha inchi seed oil reported in Table 1 shows that this oil is highly unsaturated (~93%). Linolenic acid (C18:3 ω-3) was the major fatty acid, followed by linoleic (C18:2 ω-6), oleic (C18:1 ω-9), palmitic (C16:0) and stearic (C18:0) acids. The fatty acid content of Sacha inchi seed oil found in this study is in agreement with the technical data provided by Industrias Amazonicas and data previously reported by Hamaker et al. [4] and Follegatti-Romero et al. [6]. The fatty acid composition of Sacha inchi seed oil is similar to that found in flax seed oil [17]. The differences between these two oils are in the ω-6:ω-3 ratio. The World Health Organization recommends a ω-6:ω-3 ratio of 5:1 to 10:1, while a ratio between 1:1 and 4:1 is often considered as optimal [18]. The ω-6:ω-3 ratio for Sacha inchi seed oil is 0.75:1, a recommended value compared to low ratios of fish oils (cod liver, 0.04:1; salmon, 0.03:1; and sardine, 0.07:1), and high ratios of some seed oils (soya, 7.05:1; olive, 11:1; and sunflower 632:1) [3]. Due to this ratio, Sacha inchi seed oil could be used for human nutrition. Interestingly, fish oil contains important unsaturated fatty acids (Eicosapentaenoic (EPA) and Docosahexaenoic (DHA) acids) not present in Sacha inchi oil. But, Sacha inchi seed oil contains linolenic acid, which can be converted to EPA and DHA by human metabolism [19]. Furthermore, Sacha inchi seed oil does not have an unpleasant taste, typical of fish oil.

High Pressure Phase Equilibria

Table 2 shows the experimental data measured for the CO_2 + Sacha inchi seed oil system for each temperature,

Table 1 Fatty acid composition of Sacha inchi oil

Fatty acid	% Area				FA content (mg/g oil)	% w/w
	This study	Technical data[a]	Follegatti-Romero et al. [6]	Hamaker et al. [4]		
Palmitic acid (C16:0)	4.08	3.65	4.24	4.50	38.95	3.90
Stearic acid (C18:0)	2.96	2.54	2.50	3.20	28.21	2.82
Oleic acid (C18:1 ω-9)	10.45	8.28	8.41	9.60	99.82	9.98
Linoleic acid (C18:2 ω-6)	35.34	36.80	34.08	36.80	337.36	33.74
Linolenic acid (C18:3 ω-3)	46.92	48.61	50.41	45.20	447.87	44.79
Gadoleic acid	0.25	–	0.16	–	2.34	0.23
Total	100.00	99.88	99.8	99.30	954.55	95.46
Saturated	7.04	6.19	6.74	7.70	67.16	6.72
Monounsaturated	10.71	8.28	8.57	9.60	102.16	10.21
Polyunsaturated	82.26	85.41	84.49	82.00	785.23	78.53

[a] Industrias Amazonicas, *n.d.* not determined, *w/w* weight/weight (g FA/g oil × 100)

Table 2 High-pressure phase transitions (P.T.) and equilibria data for CO_2 + Sacha inchi oil

x_{CO_2}	T (K)					
	303		313		323	
	P (MPa)	P.T.	P (MPa)	P.T.	P (MPa)	P.T.
0.7488	4.286	LV	5.061	LV	5.836	LV
0.7876	5.161	LV	6.161	LV	7.161	LV
0.8322	6.181	LV	7.471	LV	8.911	LV
0.8691	7.051	LV	9.199	LV	11.546	LV
0.8948	11.651	LLV	13.111	LL	15.521	LL
0.9145	22.560	LL	23.231	LL	24.531	LL
0.9994	27.720	LL	–	LL	–	LL
0.9994	24.740	LL	–	LL	–	LL
0.9995	24.291	LL	–	LL	–	LL
0.9996	24.180	LL	25.540	LL	27.110	LL
0.9996	22.230	LL	25.290	LL	27.390	LL
0.9997	20.860	LL	22.810	LL	24.880	LL

T, pressure, *P*, and mole fraction of CO_2, x_{CO_2}. This table also reports phase transitions experimentally observed, where the CO_2 mole fraction varied from 0.7488 to 0.9997. With an increment of both CO_2 mole fraction and pressure, phase transitions were observed for each isotherm. For example, at 313 and 323 K, phase transitions from liquid-vapor (LV) to liquid-liquid (LL) were observed when increasing the CO_2 mole fraction from 0.8691 to 0.8948. Further increase in pressure and CO_2 mole fraction will result in a CO_2 rich phase (LL) for the three isotherms studied.

Figure 1 shows that at $x_{CO_2} = 0.8948$, liquid-liquid-vapor (LLV) is first observed in one experimental point at 303 K. At a constant pressure, increasing the CO_2 mole fraction, it was observed phase transitions from liquid to LV or from liquid to LL. The LL phase is rich in CO_2, while the liquid phase is rich in oil. Figures 1 and 2 show dashed lines for visualization purpose of the phase transition limits observed experimentally.

Figure 2 shows that the phase behavior of supercritical CO_2 + Sacha inchi seed oil is similar to that of supercritical CO_2 + soybean oil [8]. However, it can be observed that CO_2 is more soluble in soybean oil than in Sacha inchi seed oil at the same temperature and pressures below 12 MPa. Even though the molar masses of both oils are similar, soybean oil [8] contains more than 175 and 125% of palmitic and oleic acids, respectively. These fatty acids, linolenic and stearic acids showed previously high absorption of CO_2 [20]. Therefore, the high solubility of CO_2 in the soybean oil can be due to the difference in fatty acid composition and its interactions with CO_2. Figure 2 also shows that the transition pressure values for Sacha inchi seed oil are higher than those obtained for soybean oil [8].

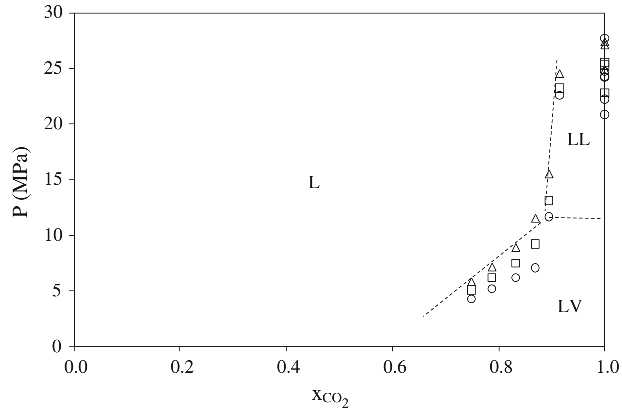

Fig. 1 Phase diagram for the binary system supercritical CO_2 + Sacha inchi oil at 303 K (*open circles*), 313 K (*open squares*), and 323 K (*upward triangles*). *Dashed lines* indicate phase transition limits observed experimentally (*broken lines*)

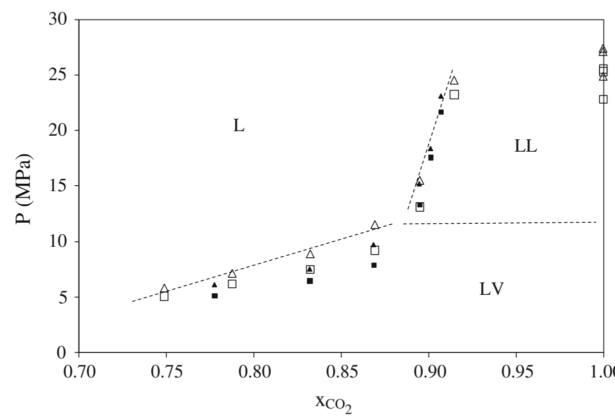

Fig. 2 Phase diagram for binary systems of supercritical CO_2 + oil. Sacha inchi seed oil at 313 K (*open squares*) and 323 K (*upward triangles*). Soybean oil at 313 K (*filled squares*) and 323 K (*filled triangles*) (data from Ndiaye et al. [8]). *Dashed lines* indicate phase transition limits observed experimentally (*broken lines*)

Figure 3 shows the pressure-temperature phase diagram at various mole fractions of soybean oil or Sacha inchi seed oil in supercritical carbon dioxide. Both systems exhibit a similar behavior at temperatures of 303, 313 and 323 K and at $x_{CO_2} = 0.9145$ (for Sacha inchi seed oil) and at $x_{CO_2} = 0.9071$ (for soybean oil).

Thermodynamic Modeling of Experimental Data

To model the experimental data, PR-EoS was used. The Sacha inchi seed oil was treated as a pseudo-pure compound for the binary system (Sacha inchi seed oil + CO_2). The composition of this pseudo-pure compound was obtained assuming that the GC composition (area percent)

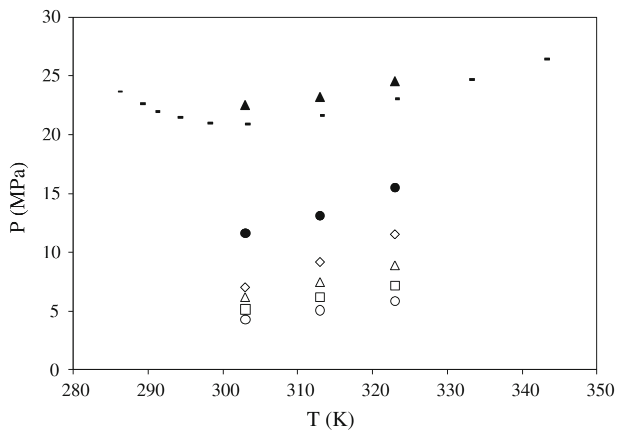

Fig. 3 Pressure versus temperature diagram for supercritical CO_2 (1) + oil (2). Sacha inchi seed oil at $x_1 = 0.7488$ (*open circles*), $x_1 = 0.7876$ (*open squares*), $x_1 = 0.8322$ (*open triangles*), $x_1 = 0.8691$ (*open diamonds*), $x_1 = 0.8948$ (*filled circles*), $x_1 = 0.9145$ (*filled triangles*). Soybean oil at $x_1 = 0.9071$ (*thick line*) (data from Ndiaye et al. [8])

can be directly converted to mass percent. Only compounds reported in Table 3 were considered. To evaluate the Sacha inchi seed oil thermophysical properties, the GC-MS data were normalized to the corresponding area percentages.

Table 3 shows the main properties of the compounds involved in this study such as the molar mass MM, the normal boiling temperature T_b, the critical temperature T_c, the critical pressure P_c, and the acentric factor ω. All data were obtained from Diadem [21]. Kay's rule was used to calculate the properties of the Sacha inchi seed oil from its main components. In order to convert the MM of Sacha inchi free fatty acids to triglycerides, the equation reported in Halvorsen et al. [22] was used. This equation uses the molar fraction and MM of each free fatty acid found in the oil to predict the average MM of triglycerides.

The LV experimental data was fitted by the PR-EoS with two temperature-independent interaction parameters ($k_{ij} = 0.0039$ and $l_{ij} = 0.3379$) and the phase behavior of the binary system was predicted by the GPEC software [23]. The average relative percent deviations in pressure for the fitted and predicted values were 34.3 and 40.0%, respectively.

The experimental data of the system CO_2 + Sacha inchi seed oil and the LL phase diagram predicted using the PR-EoS at 303 and 323 K are shown in Fig. 4.

The predicted global phase diagram (Fig. 5) and the data of Table 3 for the CO_2 + Sacha inchi seed oil binary system indicate a type V phase behavior according to the classification of Konynenburg and Scott [24].

The deviations obtained using this model agree well with deviations reported for other oil systems in CO_2 [25]. The thermodynamic model was able to predict qualitatively the phase behavior of the system studied. Furthermore, the predicted low solubility of the oil in the compressed-gas phase agrees well with the experimental data. However, the deviation between experimental and predicted data for the phase behavior becomes evident as the cubic PR-EoS cannot provide exact predictions for Sacha inchi seed oil that is a complex macromolecule composed by a mixture of triglycerides.

Conclusions

This study provided new experimental data of phase behavior of Sacha inchi seed oil in carbon dioxide at 303, 313 and 323 K, and pressures from 4 to 28 MPa. This oil can be used as a functional food ingredient due to its high content of omega-3 fatty acid (46.92%) and PUFA content (82.26%). The system CO_2 + Sacha inchi seed oil showed LV, LL and LLV phase transitions. Furthermore, CO_2 was more soluble in soybean oil than in Sacha inchi seed oil due to its different fatty acid composition and its interactions with CO_2. The prediction of the phase behavior using PR-EoS with the van

Table 3 Sacha inchi oil normalized mass composition and main fatty acids, and pseudo-critical properties and acentric factor of Sacha inchi oil and CO_2

Compound	Normalized mass fraction	MM (g/mol)	T_b (K)	T_c (K)	P_c (MPa)	ω
Palmitic acid	0.0410	256.43	624.15	785.00	1.510	0.9827
Stearic acid	0.0296	284.48	648.35	804.00	1.360	1.0360
Oleic acid	0.1048	282.47	633.00	781.00	1.390	1.1820
Linoleic acid	0.3543	280.45	628.00	775.00	1.410	1.1800
Linolenic acid	0.4703	278.44	632.00	780.00	1.440	1.1870
Sacha inchi oil	–	874.33[a]	630.85	779.25	1.425	1.1712
CO_2	–	44.01	–	304.21	7.383	0.2236

[a] Calculated by an equation reported in Halvorsen et al. [22]

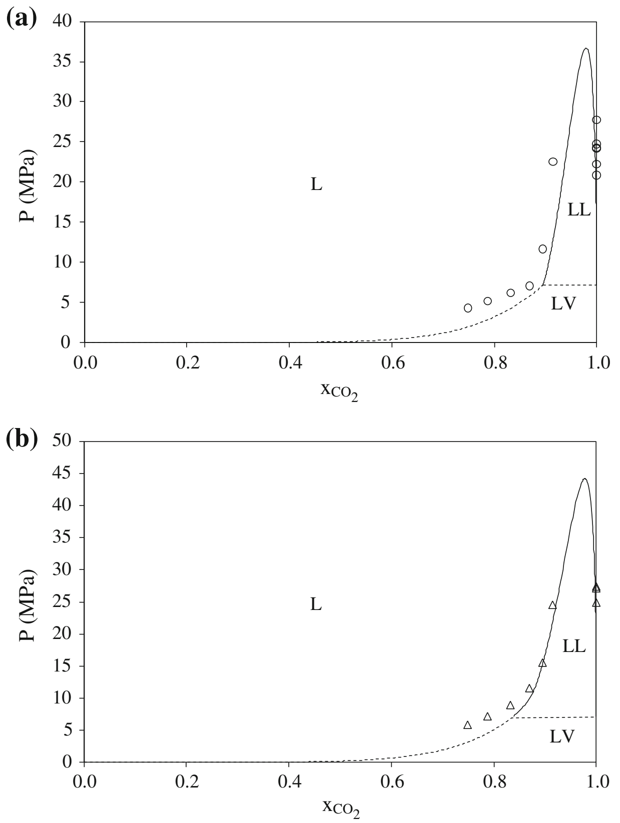

Fig. 4 Phase diagram for the binary system CO_2 + Sacha inchi seed oil at: (**a**) 303 K, and (**b**) 323 K. The parameters used to predict the phase equilibrium were $k_{12} = 0.0039$ and $l_{12} = 0.3379$

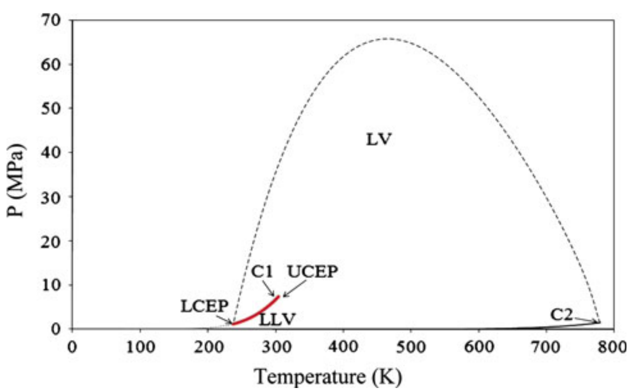

Fig. 5 Pressure versus temperature global phase diagram predicted for the binary system CO_2 + Sacha inchi seed oil. *C1* CO_2 critical point, *C2* Sacha inchi seed oil critical point, *LV* liquid-vapor equilibria, *LLV* liquid-liquid-vapor equilibria *thick line*), *UCEP* upper critical end point, *LCEP* lower critical end point, critical points of the binary mixtures (*broken lines*), vapour pressure of pure CO_2 (*dotted line*), and vapour pressure of Sacha inchi seed oil (*thin line*)

der Waals quadratic mixing rule showed a deviation below 40% for the experimental data obtained using two temperature-independent interaction parameters. In addition, the model was able to predict the global phase behavior of CO_2 + Sacha inchi seed oil system.

Acknowledgment The authors are grateful to Natural Science and Engineering Research Council of Canada (NSERC) for financial support of this project and CAPES/PROCAD-NF.

References

1. Shahidi F (2009) Nutraceuticals and functional foods: whole versus processed foods. Trends Food Sci Tech 20:376–387
2. Perez-Martinez P, Perez-Jimenez F, Lopez-Miranda J (2010) n-3 PUFA and lipotoxicity. Biochim Biophys Acta 1801:362–366
3. Rubio-Rodríguez N, Beltrán S, Jaime I, de Diego SM, Sanz MT, Carballido JR (2010) Production of omega-3 polyunsaturated fatty acid concentrates: a review. Innov Food Sci Emerg 11:1–12
4. Hamaker BR, Valles C, Gilman R, Hardmeier RM, Clark D, Garcia HH, Gonzales AE, Kohlstad I, Castro M, Valdivia R, Rodriguez T, Lescano M (1992) Amino acid and fatty acid profiles of the Inca peanut (*Plukenetia volubilis* L.). Cereal Chem 69:461–463
5. O'Brien RD (2009) Fat and oils: formulating and processing for applications, 3rd edn. Taylor & Francis, Boca Raton
6. Follegatti-Romero LA, Piantino CR, Grimaldi R, Cabral FA (2009) Supercritical CO_2 extraction of omega-3 rich oil from Sacha inchi (*Plukenetia volubilis* L.) seeds. J Supercrit Fluid 49:323–329
7. Temelli F (2009) Perspectives on supercritical fluid processing of fats and oils. J Supercrit Fluid 47:583–590
8. Ndiaye PM, Franceschi E, Oliveira D, Dariva C, Tavares FW, Vladimir Oliveira J (2006) Phase behavior of soybean oil, castor oil and their fatty acid ethyl esters in carbon dioxide at high pressures. J Supercrit Fluid 37:29–37
9. Riha V, Brunner G (1999) Phase equilibrium of fish oil ethyl esters with supercritical carbon dioxide. J Supercrit Fluid 15:33–50
10. Peng DY, Robinson DB (1976) A new two-constant equation of state. Ind Eng Chem Fund 15:59–64
11. Brennecke JF, Eckert CA (1989) Phase equilibria for supercritical fluid process design. AIChE J 35:1409–1427
12. Souza AT, Benazzi TL, Grings MB, Cabral V, Antônio da Silva E, Cardozo-Filho L, Ceva Antunes OA (2008) Supercritical extraction process and phase equilibrium of candeia (*Eremanthus erythropappus*) oil using supercritical carbon dioxide. J Supercrit Fluid 47:182–187
13. Moura LS, Favareto R, Leal PF, Corazza ML, Cardozo-Filho L, Meireles MAA (2009) Phase equilibrium measurements for CO_2 + priprioca extract at high pressures. J Supercrit Fluid 48:126–130
14. Takeuchi TM, Leal PF, Favareto R, Cardozo-Filho L, Corazza ML, Rosa PTV, Meireles MAA (2008) Study of the phase equilibrium formed inside the flash tank used at the separation step of a supercritical fluid extraction unit. J Supercrit Fluid 43:447–459
15. Alvarez VH, Larico R, Ianos Y, Aznar M (2008) Parameter estimation for VLE calculation by global minimization: genetic algorithm. Braz J Chem Eng 25:409–418
16. Alvarez VH, Aznar M (2008) Vapor–liquid equilibrium of binary systems ionic liquid + supercritical CO_2 or CHF_3 and ionic liquid + hydrocarbons using the Peng–Robinson equation of state. J Chin Inst Chem Eng 39:353–360
17. Quispe-Condori S, Saldaña MDA, Temelli F (2011) Microencapsulation of flax oil with zein using spray and freeze drying. LWT Food Science and Technology. doi:10.1016/j.lwt.2011.01.005
18. WHO/FAO Fats and oils in human nutrition. http://www.fao.org/docrep/v4700e/v4700e00.htm. Accessed Nov. 2010

19. Calder PC, Yaqoob P (2009) Omega-3 polyunsaturated fatty acids and human health outcomes. Biofactors 35:266–272
20. Penedo GL, Coelho V, Mendes MF (2009) Phase equilibria of oleic, palmitic, stearic, linoleic and linolenic acids in supercritical CO_2. Braz J Chem Eng 26:137–147
21. Diadem Public v.1.2 (2000) The DIPPR information and data evaluation manager
22. Halvorsen JD, Mammel WC Jr, Clements LD (1993) Density estimation for fatty acids and vegetable oils based on their fatty acid composition. J Am Oil Chem Soc 70:875–880
23. Cismondi M, Michelsen ML, Zabaloy MS (2008) Automated generation of phase diagrams for binary systems with azeotropic behavior. Ind Eng Chem Res 7:9728–9743
24. Prausnitz JM, Lichtenthaler RN, Gomes de Azevedo E (1999) Molecular thermodynamics of fluid-phase equilibria, 3rd edn. Prentice Hall, Upper Saddle River
25. Valderrama JO, Alvarez VH (2004) Phase equilibrium in supercritical CO_2 mixtures using a modified Kwak-Mansoori mixing rule. AIChE J 50:480–488