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Cocoa Butter Saturated with Supercritical Carbon Dioxide: Measurements and Modelling of Solubility, Volumetric Expansion, Density and Viscosity

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Cocoa Butter Saturated with Supercritical Carbon Dioxide: Measurements and Modelling of Solubility, Volumetric Expansion, Density and Viscosity*

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Abstract

The use of supercritical carbon dioxide technology for lipid processing has recently developed at the expense of traditional processes. For designing new processes the knowledge of thermophysical properties is a prerequisite. This work is focused on the characterization of physical and thermodynamic properties of CO₂-cocoa butter (CB) saturated mixture. Measurements of density, volumetric expansion, viscosity and CO₂ solubility were carried out on CB-rich phase at 313 and 353 K and pressures up to 40 MPa. The experimental techniques have previously been compared and validated. Density measurements of CB and CB saturated with CO₂, were performed using the vibrating tube technology at pressures ranging from 0.1 to 25 MPa. Experimental values correlated well with the modified Tait equation. CO₂ solubility measurements were coupled to those of density in the same pressures ranges. At 25 MPa, the solubility of CO₂ is 31.4 % and 28.7 % at 313 and 353 K. Phase behaviour was investigated using a view cell in order to follow the expansion of the CB-rich phase with the rise in pressure. Volumetric expansion up to 47 % was measured and correlated to the CO₂ solubility. Phase inversion was observed at 313 K and 40 MPa. Lastly, we developed an innovative falling ball viscometer for high pressure measurements. Viscosity measurements were carried out up to 25 MPa showing a viscosity reduction up to 90 % upon CO₂ dissolution. These results were correlated with two empirical models. A new model here presented, was favourably compared with the Grunberg and Nissan model. All the experimental results are consistent with the available literature data for the CB-CO₂ mixture and other fat systems. This work is a new

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contribution to the characterization of physical and thermodynamic behaviour of fats in contact with CO₂ which is necessary to design supercritical fluid processes for fats processing.

KEYWORDS: phase equilibrium, density, viscosity, modelling, cocoa butter, supercritical CO₂

1. Introduction

Supercritical fluid processes are emerging technologies, which are clean and efficient alternative to conventional methods for fats and oils processing (Temelli, 2009). Supercritical carbon dioxide (SC-CO₂) is commonly used and has become the solvent of choice for food, cosmetic and pharmaceutical industries, because of its non toxicity and its moderate critical properties (critical pressure: 7.38 MPa, critical temperature: 304.35 K). Several studies over the last twenty years were dedicated to the supercritical extraction and fractionation of fats and oils of vegetable and animal origin. These applications could allow isolating added value lipids such as polyunsaturated fatty acids, tocopherols, carotenoids, phytosterols known for their health benefits (Sahena *et al.*, 2009).

Cocoa butter (CB) is a complex natural product composed of different types of triglycerides (TG) whose proportions vary according to its geographic origin (Chaiseri and Dimick, 1989). The most abundant ones are monounsaturated TG, which have the unsaturated fatty acid in the 2-position and saturated fatty acids in 1- and 3-position: 1-palmitoyl-2-oléoyl-3stéaroylglycérol (POS), 1,3-stéaroyl-2-oléoylglycérol (SOS) and 1,3-palmitoyl-2oléoylglycérol (POP). CB is the fat of cocoa and it is used in the chocolate manufacturing process. Considering chocolate crystallization, the TG are mainly responsible of the polymorphic transitions at different temperatures. Indeed, the CB can crystallize in six different polymorphic forms (in order of increasing stability): I (melting point, 286.1-290.6 K), II (290.8-292.9 K), III (295.4-297.5 K), IV (299.4-300.9 K), V (303.7-307.4 K) and VI (306.8-307.1 K). In addition, the polymorphic fraction of each form has a direct influence on the quality and the characteristics of the end product. Supercritical crystallisation of CB has already been investigated (Letourneau *et al.*, 2005; Perva-Uzunalic *et al.*, 2008) and led to the successful generation of form V crystals. Venter *et al.* (2006) investigated the gas assisted mechanical expression (GAMSE) process consisting in pressing mechanically cocoa nibs saturated with supercritical CO₂, in order to produce CB. The supercritical fractionation of CB has not yet been fully investigated though Bhaskar *et al.* (1996) were the first to show that it was feasible. They used the difference of solubility in CO₂ of the three predominant triglycerides contained in CB.

This work is the preliminary step of a study aiming at a new clean recrystallization / fractionation process of CB assisted by SC-CO₂. As any other process design, it requires the knowledge of properties of the CO₂-CB mixture such as reciprocal solubility, phase equilibria behaviour, density and viscosity of phases. They are necessary to go further in the understanding of the phenomena implied in the processing of lipids. Yet, there is a lack of such physical and thermodynamic properties data in the literature.

This study has been limited to the liquid phase composed of melted CB saturated with CO₂ and for which we carried out experimental and modelling work of the density and viscosity. Moreover, we investigated the phase equilibria behaviour by the determination of the CO₂ solubility and the volumetric expansion of CB saturated with CO₂. These characterization techniques were validated by comparing the measured properties of CO₂-DMSO mixture with available literature data (Calvignac *et al.*, 2009a).

2. Material and Methods

2.1. Materials

Cocoa butter was obtained from Gerkens Cacao (Wormer, The Netherlands). It comes from the same supplier and the same origin as the cocoa butter used by Venter *et al* (2006). Its composition is given in Table 1. Carbon dioxide (purity 99.995 %) was purchased from Air liquide S.A. (Paris, France). Pure water was obtained by ELGA purification system.

Table 1. Composition in triglycerides of cocoa butter. O, L, P, S and A stand respectively for the following fatty acids: oleic, linoleic, palmitic, stearic and arachidic

Triglycerides	Composition (%)
OLO	0.4
PLP	0.4
OOO	1.5
POO	0.3
PLS	1.8
POP	18.0
POS	38.2
SOS	26.0
SOO	1.8
SLS	2.4
PPS	4.7
PSS	3.1
SOA	1.1
SSS	0.3

2.2. Experimental set-up and procedures

2.2.1. Solubility and density measurements

A photograph and a schematic diagram of the static analytical device for VLE and density measurements are shown in Figure 1 and 2.

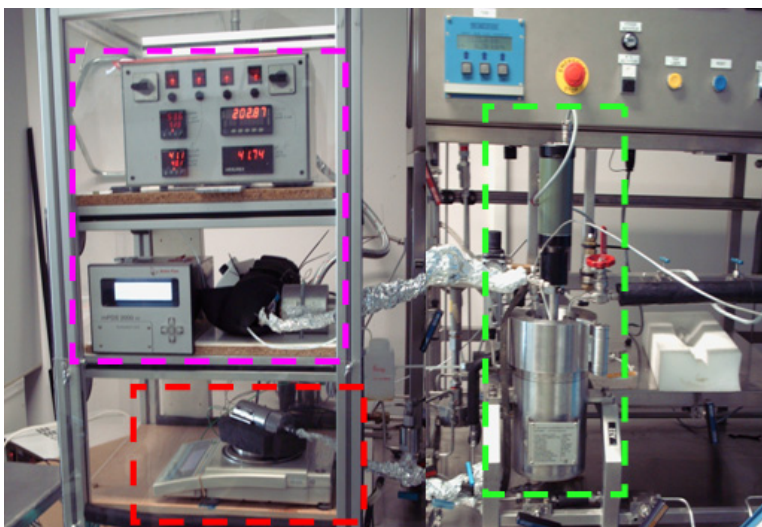


Figure 1. Photograph of the experimental device

The apparatus has been designed to carry out investigations under high pressure and high temperature, respectively up to 35 MPa and 473 K. It is composed of three main parts: a VLE device, a gravimetric analysis device and a densimeter. A similar device for VLE measurements was used in a previous study dedicated to the development and to the validation of this experimental set-up (Calvignac *et al.*, 2009a).

The stainless steel autoclave (1), which capacity is 500 mL (Xenard, France), was previously loaded with 250 mL of melted CB and heated to the desired temperature. Liquid CO₂ was pumped by a high pressure membrane pump (Lewa, France) (2) and preheated by a heat exchanger (Separex, France) (3) before feeding the autoclave equipped with a stirring mechanical device (Top-industrie, France). Then, a syringe pump (Model ISCO 260D) (4) previously filled with CO₂ (260mL) and operating at the same pressure and temperature conditions as the autoclave, was used to maintain the equilibrium of the studied mixture.

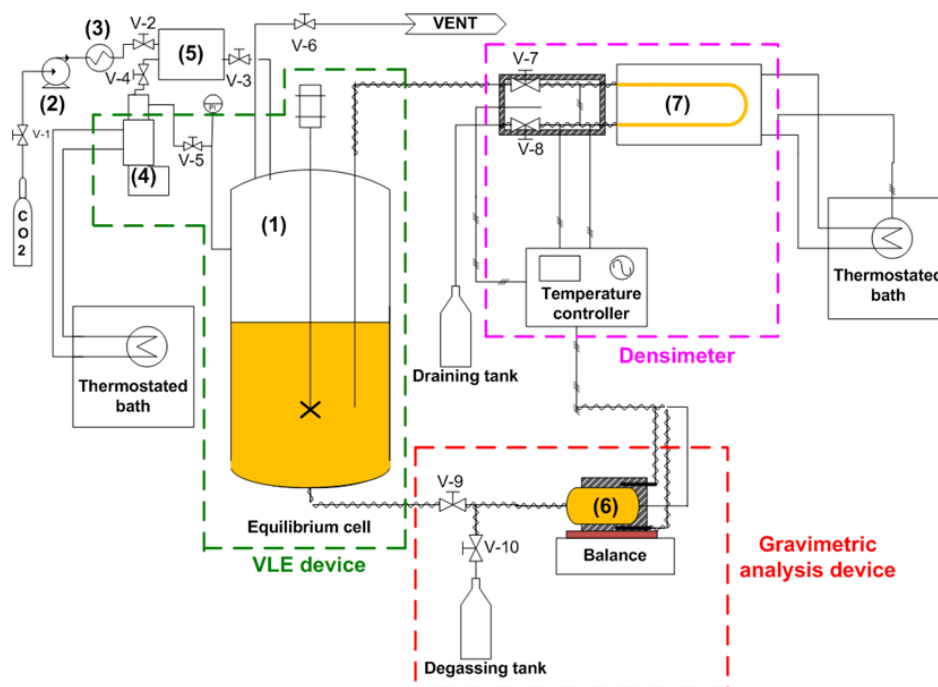


Figure 2. Schematic diagram of the VLE apparatus

The pressure and temperature set-up of the VLE apparatus (autoclave and syringe pump) were kept constant respectively within ± 0.01 MPa and ± 0.1 K. A buffer storage tank (5) is connected to the CO₂ feed pipe, to the equilibrium autoclave and to the syringe pump. Once the equilibrium was reached, pressure in the tank was increased of 5 MPa above the equilibrium pressure in order to ensure a pressure drop compensation when valve V-9 was opened to make gravimetric analysis.

Then, the compensation operation was achieved by the membrane pump. The CO₂ flow compensation was fixed to 2 kg.h⁻¹ in order to minimize the pressure drop ($\Delta P_{\max} = 0.5$ MPa) manually controlled by V-7. Cell temperature was kept constant by means of a PID controller within ± 0.1 K. This stainless steel measurement cell (Top-industrie, France) (6) was previously weighed empty and placed on a high precision balance (Sartorius Model LA3200B), and it was then used to sample 50 mL of the liquid phase. The balance used allows gravimetric analyses within ± 0.01 g. Moreover, density measurements were carried out in the same time with an accuracy of ± 0.01 kg.m⁻³. Thus, valve V-7 was opened to refill the vibrating U-tube densimeter (Anton-Paar, model DMA-HPM) (7). Temperature in the vibrating U-tube was precisely controlled by a thermostated bath within ± 0.01 K and pressure was measured by a transducer (Model Druck PTX 611) with an accuracy of ± 0.001 MPa.

Volume within the loop remaining small, equilibrium was hardly perturbed and reached quickly. All pipes of the apparatus were thermally controlled within $\pm 0.1\text{K}$.

Once all parameters (pressure, temperature, mass) were stable, they were recorded and valve V-9 was closed to isolate the cell. The valve V-10 was then opened and the mixture was slowly degassed in order to recover cocoa butter and consequently to deduce the solubility of CO_2 in the liquid phase. Then, after each experiment, the gravimetric analysis device was cleaned.

In this work, the solubility of CO_2 was defined as the mass percentage of CO_2 (X_{CO_2}) contained in the liquid phase rich in CB, according to:

$$X_{\text{CO}_2}(\%) = \frac{m_{\text{mixture}} - m_{\text{CB}}}{m_{\text{mixture}}} \cdot 100 \quad (1)$$

The vibrating U-tube densimeter was previously calibrated with water and CO_2 for all the pressure and temperature range of the VLE measurements. The principle of density measurements using this technology is based on the dependence of the vibration period of the U-bended part of the tube according to the filling fluid mass and the U-tube mass. The behaviour of the vibrating tube can be compared to an undamped spring-mass, defined by its oscillation period, τ (s), such as:

$$\tau = 2\pi \sqrt{\frac{m_0 + V\rho}{D}} \quad (2)$$

where m_0 is the mass of the empty U-tube (kg), V is the internal volume of the tube (m^3), ρ is the density of the fluid ($\text{kg}\cdot\text{m}^{-3}$) and D is the spring constant ($\text{N}\cdot\text{m}^{-1}$). Rearrangement of this equation leads to a simple relation giving the density commonly used in the vibrating tube technology:

$$\rho = A\tau^2 - B \quad (3)$$

The apparatus parameters A and B are defined from measured oscillation periods at fixed pressure and temperature conditions and known densities of water (Wagner and Pruss, 2002) and carbon dioxide (Span and Wagner, 1996), such as:

$$A = \frac{\rho_{\text{H}_2\text{O}(T,P)} - \rho_{\text{CO}_2(T,P)}}{(\tau_{\text{H}_2\text{O}(T,P)})^2 - (\tau_{\text{CO}_2(T,P)})^2} \quad (4)$$

$$B = \frac{(\tau_{CO_2(T,P)})^2 \rho_{H_2O(T,P)} - (\tau_{H_2O(T,P)})^2 \rho_{CO_2(T,P)}}{(\tau_{H_2O(T,P)})^2 - (\tau_{CO_2(T,P)})^2} \quad (5)$$

The measured oscillation periods and consequently the measured densities are very sensitive to pressure and temperature variations. Thanks to the compensation of the syringe pump (about ± 0.1 mL/min) and the good precision of the several heating devices of the VLE apparatus, the thermodynamic equilibrium can be easily reached and maintained. Each experimental point was performed at least three times with an overall precision of ± 0.60 kg.m⁻³.

The procedure for the density measurements of cocoa butter without carbon dioxide was the following: liquid cocoa butter was pumped by an ISCO syringe pump and injected into the densimeter.

2.2.2. Volumetric expansion measurements

A schematic diagram of the experimental device for volumetric expansion measurements is shown in Figure 3. The apparatus (Sitec, Switzerland) has been designed to perform experiments at pressures and temperatures up to, respectively, 50 MPa and 473 K. The experimental procedure has been validated previously (Calvignac et al., 2009a).

The cell measurement was equipped with a heating jacket and two opposite sapphire windows: one for lighting and the other for the visualization of the volumetric expansion using a digital camera. The stainless steel cell was a vertical hollow cylinder with a total volume of 93.89 ± 0.10 ml (including pipes). The pressure in the apparatus was kept constant within ± 0.1 MPa. The cell temperature was controlled precisely (± 0.2 K) with a thermostated bath by means of a PT100 temperature probe. In addition, a magnetic stirrer homogenised the mixture until the thermodynamic equilibrium was reached, that was at least one hour after stabilization of the pressure at constant temperature. The volumetric expansion measurement consisted in observing and recording the evolution of the liquid phase volume with pressure. This volume was calculated as a function of the height of liquid, which was obtained by the analysis of the captured images with the ImageJ software (National Institute of Health, USA). Note that the measurement of the height of liquid was estimated to be accurate within ± 4 pixels. As for the determination of the volumetric expansion (E) of the liquid phase, an initial volume (V_0) of CB was introduced into the cell at given temperature (T) and atmospheric pressure (P_0) by the syringe pump. Then, CO₂ was introduced at the same temperature (T) and pressure (P) by the piston pump. The mixture was

homogenised until all experimental parameters were stabilised (T, P and E) meaning that the thermodynamic equilibrium was reached.

Besides, the volumetric expansion of the liquid phase at (T) and (P) was defined by:

$$E(\%) = \frac{V(T, P) - V_0(T, P_0)}{V_0(T, P_0)} \cdot 100 \quad (6)$$

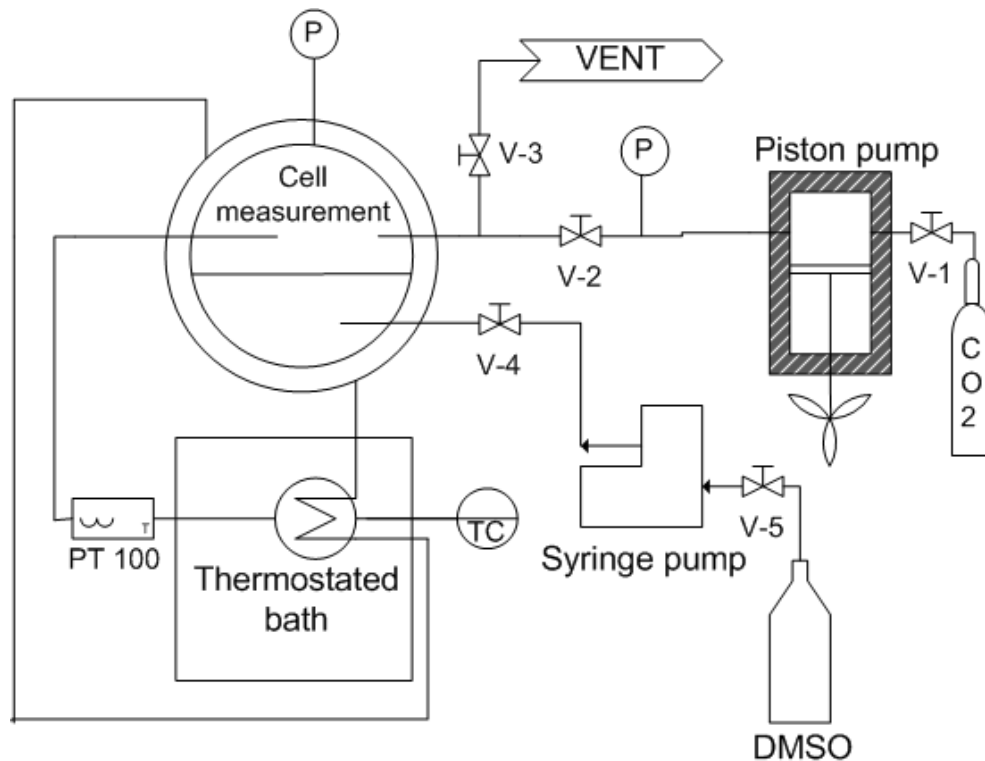


Figure 3. Schematic diagram of the apparatus for volumetric expansion measurements

2.2.3. Viscosity measurements

A schematic diagram of the falling body viscometer (FBV) is shown on Figure 4. The apparatus has been designed to perform experiments at pressures and temperatures up to, respectively 45 MPa and 473 K. The stainless steel autoclave with a capacity of 2.6 l (Top-industrie, France) was previously loaded with CB

and heated to the desired temperature. It was equipped with sapphire windows (SW) for visualization purpose using a cold lighting device and a high speed digital video camera (Photron, USA) connected to a computer. Liquid CO_2 was pumped with a high pressure membrane pump (Lewa, France) and preheated by a heat exchanger (Separex, France) before flowing into the autoclave equipped with a mechanical stirrer (Top-industrie, France). Then, a syringe pump (ISCO Model 100HLX) previously filled with CB and operating at the same temperature as in the autoclave, adjusted the level of the liquid phase (because of its expansion) so as to immerse entirely the glass tube. The pressure and temperature set-up of the viscometer were kept constant within ± 0.1 MPa and ± 0.1 K.

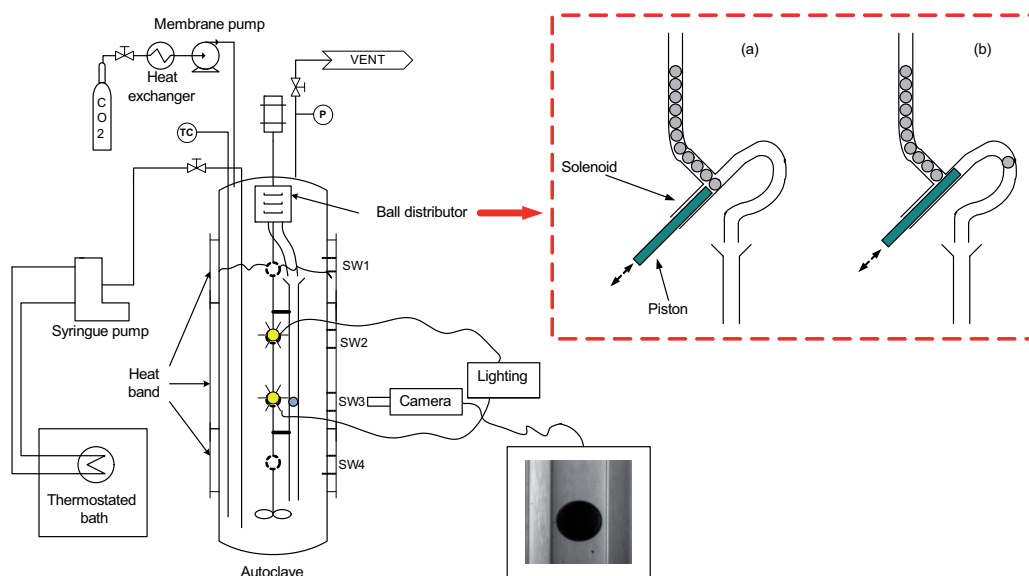


Figure 4. Schematic diagram of the high pressure viscometer

Once the equilibrium was reached, stirring was stopped and viscosity measurements were performed at constant pressure and temperature. Measurements consisted in recording through a window (SW3) the fall of an aluminium ball (2 mm diameter) in an open glass tube (2.1 mm diameter and 20 cm length). The ball distributor allowed to release them one at a time by means of an electrical impulsion given to the solenoid (Figure 4(a) and 4(b)). The first ones were not considered and ensured the homogenization of the fluid in the tube, even if the whole volume in the autoclave was previously homogenized during 24 hours.

A detailed description of the methodology for viscosity determination by CFD calculation under COMSOL Multiphysics[®] has recently been reported

elsewhere (Calvignac *et al.*, 2009b). Calculations were based on the laminar Navier-Stokes model for a newtonian fluid and on the continuity equation for an incompressible fluid, both in steady-state conditions. The key experimental parameters for these calculations were the ball terminal velocity, the fluid density and the ball density. The terminal velocities were obtained by the analysis of the images of a high-speed digital video using software developed with the Image Processing Toolbox from Matlab[®]. The fluid density data were taken from the measurements done in this work. The density of the aluminium ball, $2723.3 \pm 0.9 \text{ kg.m}^{-3}$, was previously determined by a He pycnometer. This FBV allowed measuring viscosities down to 2 mPa.s. This limitation is due to the restricted operating conditions of the technique and to the calculation model hypotheses: transparent medium, ball velocity measurable below 35 mm.s^{-1} and laminar and steady flow.

Prior to these measurements, we performed rheological measurements at atmospheric pressure on CB with a dynamic rotational rheometer (Haake Rheostress 600, Thermo electron, Germany) with a cone-plate geometry (1° angle cone and 60 mm diameter). They allowed measuring viscosity of CB from 313 to 353 K. Measurements were compared to the results obtained with the falling body viscometer (FBV) and to the literature data.

3. Results and Discussion

3.1.1. Solubility of CO₂

Solubility of CO₂ in CB was measured at 313 and 353 K. Results obtained are presented in Table 2 and Figure 5. Several investigators have also studied the phase equilibrium behaviour of CB-CO₂ binary at 313 K and 353 K (Kokot *et al.*, 1999; Venter *et al.*, 2007) and the data are presented in Figure 6 and 7. Kokot *et al.* determined the mutual solubility of CB and CO₂ using a static analytical method which consisted in sampling the heavy (rich in CB) and the light phase (rich in CO₂). Each sample was degassed and the amount of CO₂ was measured by a flow meter while the amount of CB was weighed. Venter *et al.* used two static analytical methods to determine the solubility of CO₂ in CB. The first one is identical to those used by Kokot *et al.* The second one consists in sampling the heavy phase in a cell and washing the recovered CB with petroleum ether in order to ensure that there is not residual dissolved CO₂.

The solubility of CO₂ increases with pressure whereas it decreases with the temperature (Figure 5). At 313 and 353 K, the solubility reaches respectively a maximum of 31.4 % and 28.7 %. Each data point in Figure 5 represents the average of measurements, which were repeated at least three times. The maximum uncertainty is about 2.7 % at 353 K and is due the random

experimental errors generated by the difficulty to keep constant pressure and temperature during the sampling operation.

Table 2. Solubility of CO₂ in CB at different pressures at 313 and 353 K

313 K		353 K	
P (MPa)	x _{CO₂} (%)	P (MPa)	x _{CO₂} (%)
5.31	11.3 ± 1.1	5.11	5.7 ± 2.7
10.19	24.1 ± 1.0	10.25	17.2 ± 2.1
15.16	27.5 ± 1.3	15.28	19.3 ± 1.8
20.16	29.6 ± 1.1	20.29	24.4 ± 2.3
25.19	31.4 ± 1.0	25.24	28.7 ± 2.7

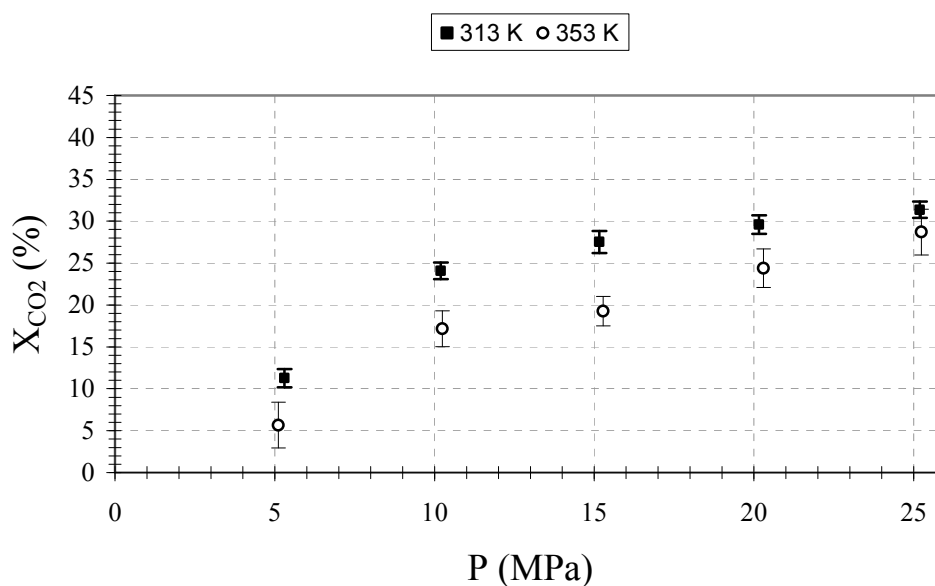


Figure 5. Evolution of CO₂ solubility in cocoa butter at 313 and 353 K

Comparisons between our experimental data and literature ones are shown in Figure 6 and 7. For both isotherms, our results are in good agreement with those of Venter *et al.* The mean deviation (MD) for results obtained with the first method is respectively 1.1 % and 1.2 % at 313 and 353 K. With regard to the second method, MD is respectively about 3.7 % and 0.8 % at 313 and 353 K. However, for both isotherms, there are significant discrepancies with data obtained by Kokot *et al.* above 7 MPa (MD=10.7 % at 313 K and 12.7 % at 353 K). It is important to note that our CB is provided by the same manufacturer than Venter *et al.* The origin of CB used by Kokot *et al.* being different, it might

influence its behaviour in contact with CO₂. We can suppose that the difference in TG composition and in the nature of minor components affect the CO₂ solubility in CB.

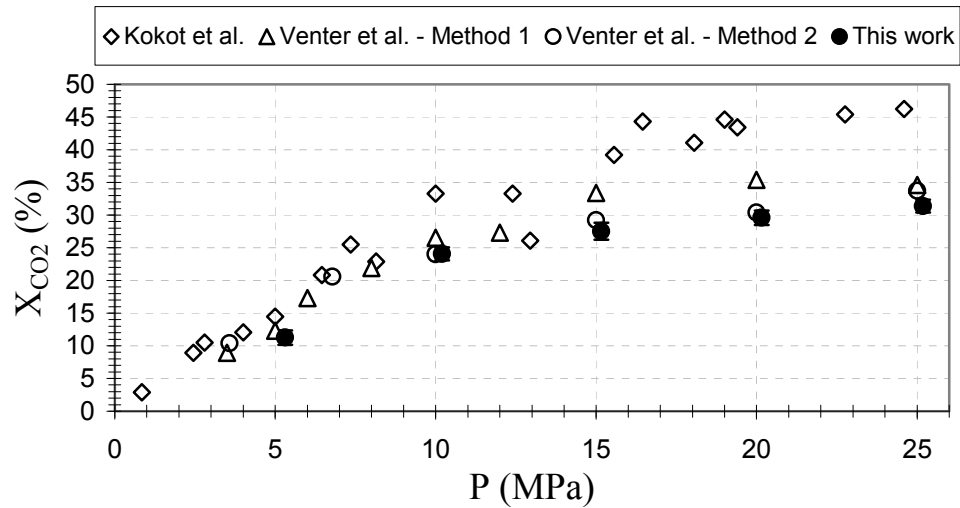


Figure 6. Comparison of CO₂ solubility in cocoa butter with literature data at 313 K

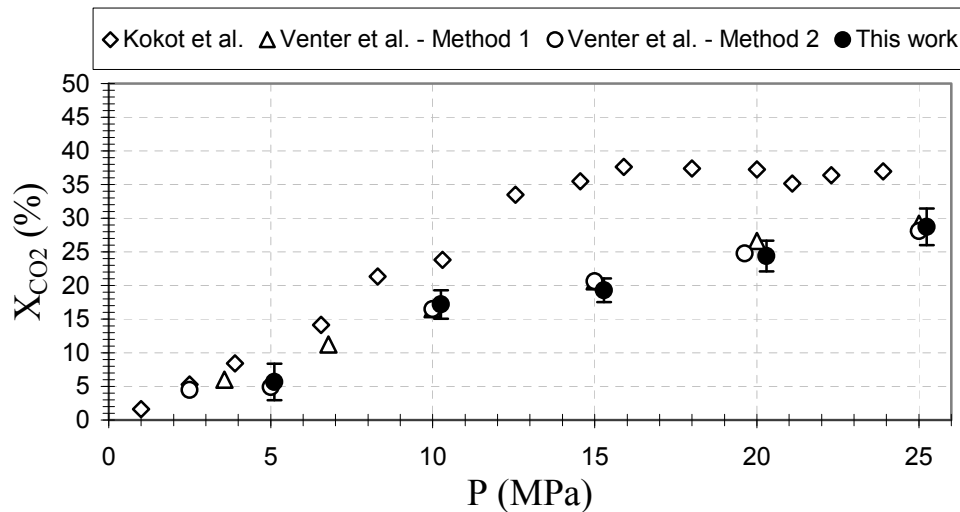


Figure 7. Comparison of CO₂ solubility in cocoa butter with literature data at 353 K

3.1.2. Density

Densities were measured for CB and CO₂-saturated CB mixture for pressure ranging from 0.1 to 25 MPa and at 313.15, 323.15 and 353.15 K. Results are presented in Table 3 and Figure 8.

Table 3. Density of cocoa butter (CB) and CB-CO₂ mixture at 313, 323 and 353 K

	313 K		323 K		353 K	
	P (MPa)	ρ (kg.m ⁻³)	P (MPa)	ρ (kg.m ⁻³)	P (MPa)	ρ (kg.m ⁻³)
CB	0.10	894.76	0.10	888.54	0.10	868.14
	5.17	897.48	5.18	891.48	5.26	871.70
	10.12	899.50	10.15	892.52	10.28	874.99
	15.19	901.84	15.14	897.68	15.28	877.06
	20.12	905.01	20.07	900.06	20.27	879.98
	25.07	908.08	25.01	902.76	25.24	883.65
CB-CO ₂ mixture	0.10	894.76	0.10	888.54	0.10	868.14
	5.41	904.70	5.19	897.22	5.21	872.87
	10.29	912.33	10.11	902.26	10.35	876.32
	15.26	920.87	15.23	910.55	15.38	881.04
	20.26	924.38	20.16	915.78	20.39	885.34
	25.29	931.48	25.08	921.62	25.34	890.22

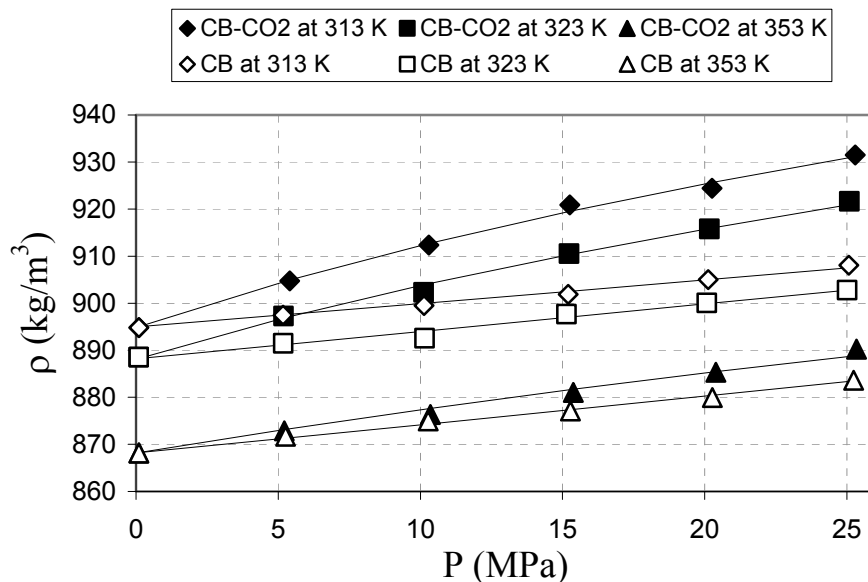


Figure 8. Density of cocoa butter (CB) and CB saturated with CO₂ at 313, 323 and 353 K and pressures up to 25 MPa

The density of cocoa butter decreases linearly with the temperature at constant pressure and conversely the density increases linearly with the pressure at constant temperature. The same behaviour for density of CB-CO₂ is observed but the slope of density increase with the pressure differs according to the temperature. However, it is more interesting to plot the CB-CO₂ mixture density versus the CO₂ solubility, since there are data available for comparison in the literature (Figure 9). At 353 K, the density increases linearly with CO₂ solubility, so is the case for the results of Venter *et al.* (2007) at the same temperature. In addition, at 313K, we can compare our results with those of Seifreid and Temelli (2009) who measured the density of fish oil and correlated it to the solubility measurements of Borch-Jensen and Mollerup (1997) for the same oil. We can see that, for both lipids, the density increase with the rising CO₂ solubility is linear up to about 25 % (33 % for Venter *et al.* results). Above this solubility value, the density increase is sharper. This leads to the conclusion that in the first linear part, density is mainly influenced by the dissolution of CO₂ while in the second part of the curve the density enhancement is mainly due to the compression effect. Hence, the dissolution of CO₂ governs the density evolution for all pressures investigated at 353 K and up to 10 MPa at 313 K. At 313 K, the range of solubility is similar for CB and fish oil, although CB is mainly composed of monounsaturated TG (C16-C18 fatty acids chain length) while fish oil is mainly composed of polyunsaturated TG (C20-C22 fatty acids chain length). It has been shown for diglycerides in literature (Sampaio de Sousa *et al.*, 2006) that the longer the fatty acids chains, the smaller the CO₂ solubility. If we suppose that it is also true for triglycerides, this would mean that the unsaturations would enhance the CO₂ solubility. Hence here the effect of the unsaturation degree might compensate a longer hydrocarbon chain length.

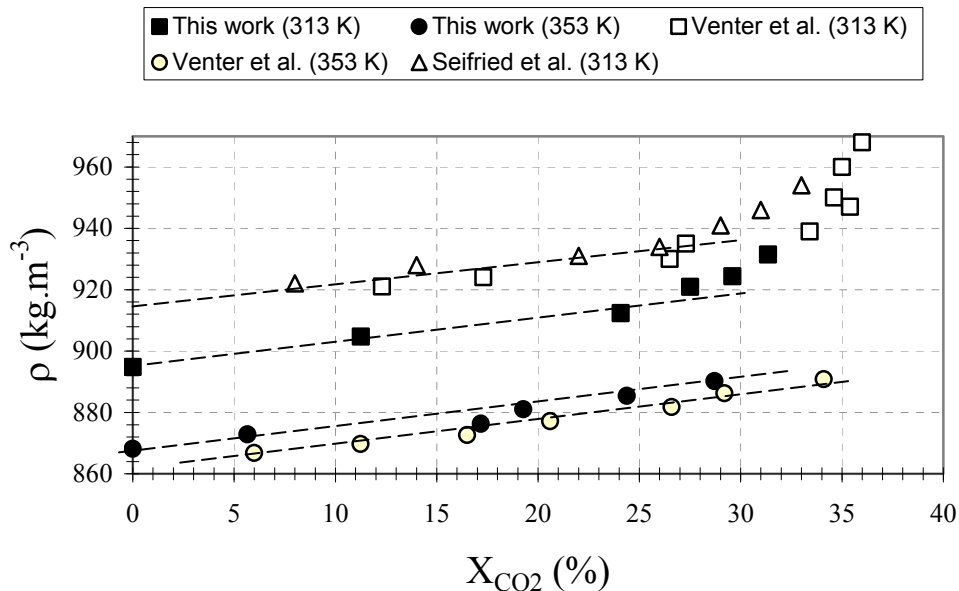


Figure 9. Comparisons of density of fats saturated with CO₂ at 313 and 353 K

The variations of density versus pressure and temperature can be represented for cocoa butter (CB) and the CO₂-saturated CB mixture using an empirical model as the modified Tait equation (Dymond and Malhotra, 1998):

$$\rho_f(T, P) = \frac{\rho(T, P_0)}{1 - C \ln \left(\frac{B(T) + P}{B(T) + P_0} \right)} \quad (7)$$

$$B(T) = B_0 + B_1 \cdot T + B_2 \cdot T^2 \quad (8)$$

where ρ_f is the fluid density (kg.m⁻³) at given pressure and temperature. $B(T)$ and C are fitting parameters without physical meaning. This empirical model has been used to fit experimental density measured at 313, 323 and 353 K and for pressure ranging from 0.1 (P_0) to 25 MPa (Table 5 and curves in Figure 8).

In order to evaluate the performance of the fitting with the Tait model, the following characteristic quantities have been used:

$$AAD = \frac{1}{N} \sum_{i=1}^{i=N} \left| 100 \cdot \left(\frac{\rho_{\text{exp}} - \rho_{\text{cal}}}{\rho_{\text{exp}}} \right) \right| \quad (9)$$

$$MaxD = Max \left(\left| 100 \cdot \left(\frac{\rho_{exp} - \rho_{cal}}{\rho_{exp}} \right) \right| \right) \quad (10)$$

$$Bias = \frac{1}{N} \sum_{i=1}^{i=N} 100 \cdot \left(\frac{\rho_{exp} - \rho_{cal}}{\rho_{exp}} \right) \quad (11)$$

Table 5. Fitting parameters and characteristics quantities for density modelling

Fluid	Modified Tait Equation
Cocoa butter (CB)	C=11.6688 $B_0=7.74510 \times 10^5$ $B_1=-4.44877 \times 10^3$ $B_2=6.52325$ AAD=0.044 % MaxD=0.174 % $Bias=2.76 \times 10^{-3}$ %
CB-CO ₂	C=0.05050 $B_0=791.54960$ $B_1=-5.11247$ $B_2=0.00847$ AAD=0.044 % MaxD=0.180 % $Bias=1.03 \times 10^{-2}$ %

The average absolute deviation (AAD) characterizes the distance between the experimental points and the modelled curve. The average deviation (Bias) characterizes the quality of the distribution of the experimental points on both sides of the modelled curve. Maximum deviation (MaxD) characterizes the maximum deviation generated by the model. In this work, we programmed the Levenberg-Marquardt algorithm under Matlab[®]. It is a very useful method for non-linear squares problem, permitting to determine the optimal combination of fitting parameters in order to minimize the deviation in relation to the experimental data. Results obtained for density fitting are satisfactory since AAD equals 0.044 %. Consequently, these results show that this model is relevant and can be used in this work as a reliable tool for viscosity determination of CB saturated with CO₂.

3.1.3. Volumetric Expansion

Expansion of cocoa butter with CO₂ was measured at 313 and 353 K and the results are presented in Table 6 and Figure 12. No volumetric expansion data about CO₂-CB system are available in the literature but some investigators characterized this property for other fats such as corn and palm oils (Tegetmeier *et al.*, 2000), fish oil (Seifreid and Temmeli, 2009).

The volumetric expansion of CB saturated with CO₂ increases with the pressure and decreases with the temperature until the inversion zone around 28 MPa. At 353 K, the expansion increases almost linearly until 25 MPa and at a slower rate at higher pressures. At 313 K the expansion curves has a hyperbolic shape tending towards a plateau reached at around 25 MPa. Indeed, above this pressure, the volumetric expansion increases only very slightly. This is linked to the density evolution comments given previously: above 10 MPa at 313 K, compression effect prevails over dissolution one. As the density of both phases increases with the pressure but not at the same rate (higher for the CO₂-rich phase), there is a pressure for which the densities are identical. At 313 K and 40 MPa, figure 13 shows that there is no longer a “heavy” and a “light” phase indicating that the density of both phases are close enough not to have one phase on top of the other. Therefore, a phase inversion has occurred at a pressure slightly lower than 40 MPa. Borch-Jensen and Mollerup (1997) observed also this phenomenon at 313 K and 42 MPa for fish oil in equilibrium with CO₂.

Table 6. Volumetric expansion of cocoa butter saturated with CO₂ at 313 and 353 K

313 K		353 K	
P (MPa)	E (%)	P (MPa)	E (%)
5.00	14.17 ± 0.45	5.08	4.63 ± 0.12
7.91	27.60 ± 0.80	8.69	10.88 ± 0.26
10.09	32.24 ± 0.92	10.27	13.50 ± 0.32
15.14	36.40 ± 1.02	15.08	22.36 ± 0.51
20.04	38.35 ± 1.06	20.07	30.82 ± 0.67
25.02	39.57 ± 1.09	25.00	36.67 ± 0.78
30.09	40.55 ± 1.11	30.04	40.90 ± 0.86
33.31	40.79 ± 1.12	35.07	44.72 ± 0.92
		40.15	47.14 ± 0.96

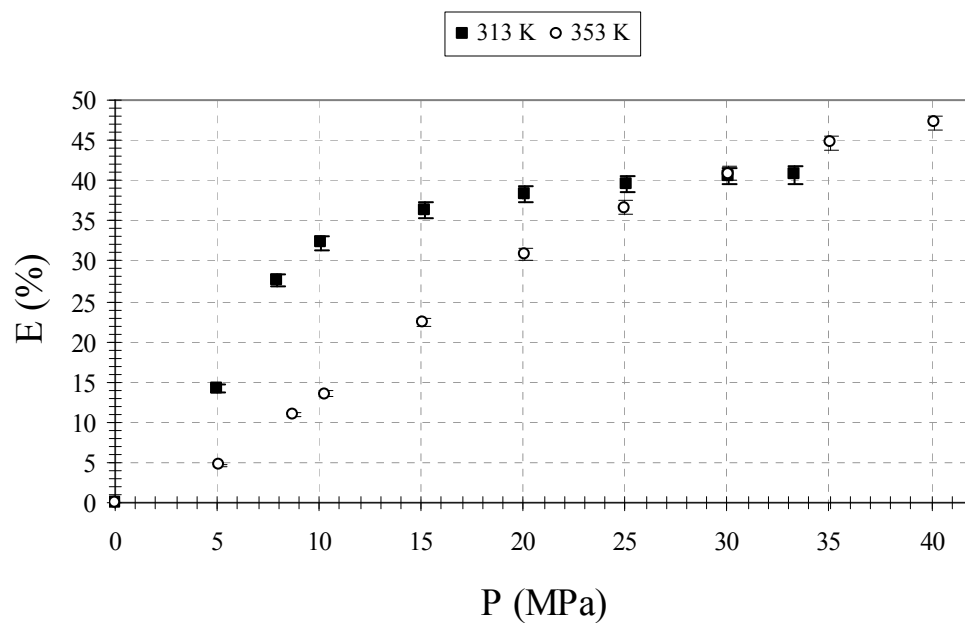


Figure 12. Volumetric expansion of CB saturated with CO_2 as a function of the pressure at 313 and 353 K

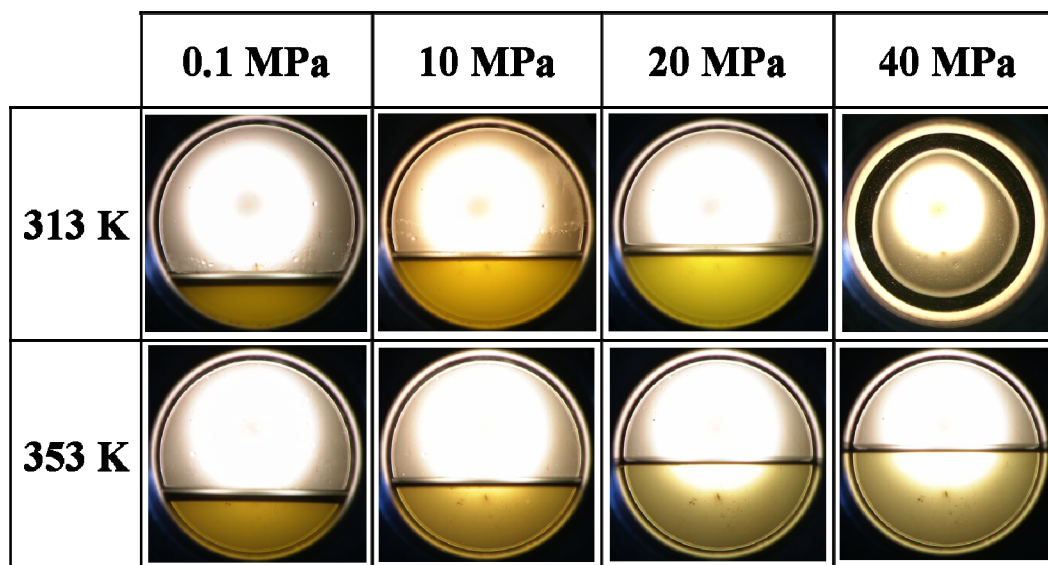


Figure 13. Phase equilibria behaviour at 313 and 353 K

The volumetric expansion increases almost linearly with the CO₂ solubility with a slope close to 1 (Figure 14). It means that other influences than the CO₂ dissolution such as temperature effect and compression are negligible within the operating range investigated.

Rigorously, volumetric expansion is linked to the CO₂ solubility and to the density of CB-rich phase (ρ_{CB-CO_2}) and CB (ρ_{CB}) following the equation (6):

$$E(\%) = \left(\frac{\rho_{CB(T,P)}}{\rho_{CB-CO_2(T,P)}} \left(\frac{1}{1 - X_{CO_2}} \right) - 1 \right) \cdot 100 \quad (12)$$

Given that we have measured independently CO₂ solubility and density of the mixture, we can then calculate volumetric expansion and compare it to the measured one. Density of CB is obtained from the Tait equation fitted on experimental values as explained above and under the same operating conditions as the CO₂ solubility ones. As it is shown in Figure 15, it turns out that the calculated values are consistent with the measured ones, except for one point at 10 MPa and 353 K for which there may have been a trouble for solubility measurement: using the solubility value at the lowest deviation value, that is 15.1 %, would fit better the measured expansion. At 313 and 353 K, MD are respectively about 1.75 and 1.69 %. Hence, the independent measures of the different properties are consistent between them. This strengthens the reliability of our measurement methods.

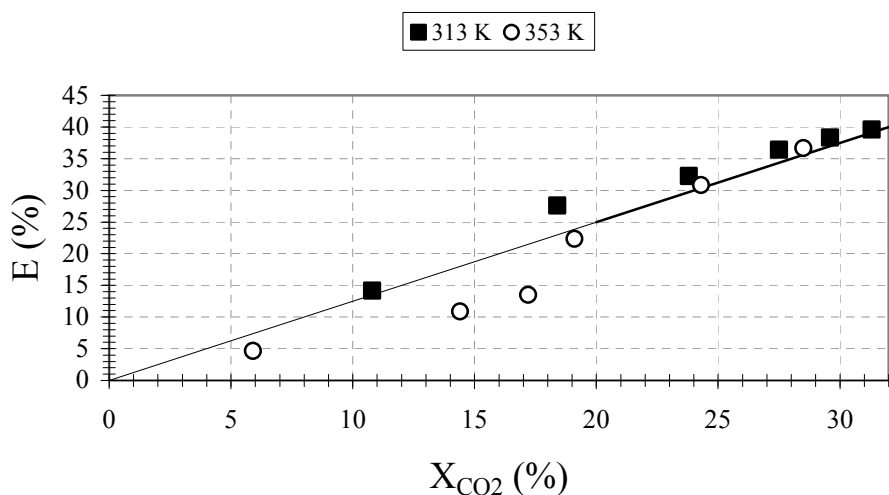


Figure 14. Evolution of the volumetric expansion of cocoa butter saturated with CO₂ with the CO₂ solubility

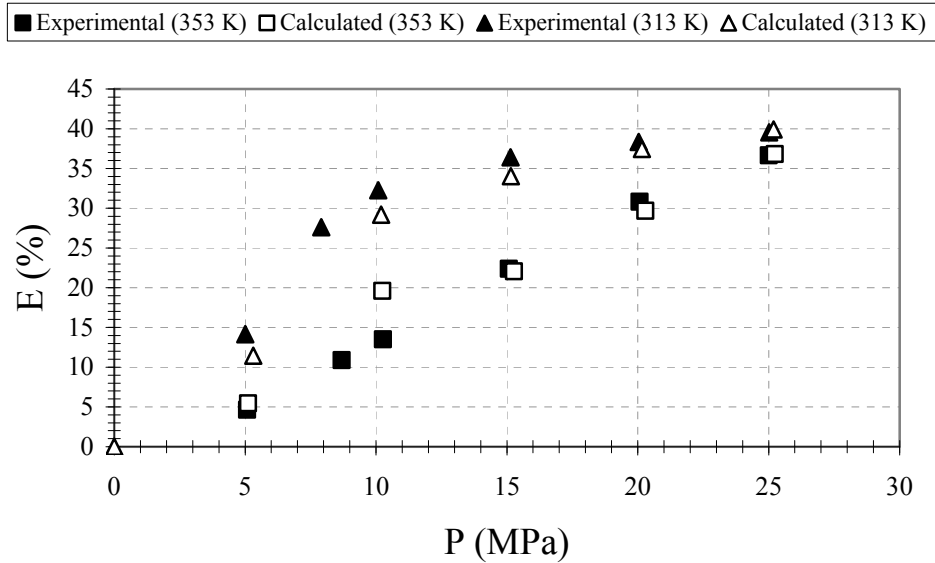


Figure 15. Comparisons of the evolution of experimental and calculated volumetric expansion with the pressure at 313 and 353 K

3.1.4. Viscosity

CB viscosity was measured for temperature ranging from 313.15 to 353.15 K at atmospheric pressure and compared to results obtained with a dynamic rotational rheometer and to the literature data (Table 7). CB is a newtonian fluid and its viscosity decreases exponentially with temperature. Figure 16 shows the comparison between the experimental data obtained with the FBV, the rheometer (MD=1.10 mPa.s) and data obtained by Venter *et al.* (MD=2.06 mPa.s). Hence, it confirms the reliability of the technique. The viscosity behaviour of CB at atmospheric pressure (P_0) can be represented with the Frenkel-Andrade model (Frenkel, 1946) which assumes that viscosity is a thermally activated process:

$$\mu_{CB}(T, P_0) = B \cdot \exp\left(\frac{E_a}{RT}\right) \quad (13)$$

where E_a represents an activation energy and B is a constant which are determined by using a curve fitting method with the Levenberg-Marquart algorithm. These parameters have been fitted with experimental values obtained with the FBV and are given in Figure 16. The equation 13 has been used to

estimate the CB viscosity which is required for the modelling work of the CB-CO₂ viscosity.

Table 7. Comparison of measured and literature values of the viscosity of cocoa butter as a function of temperature at atmospheric pressure

T (K)	μ (mPa.s)		
	This work (FBV)	This work (Rheometer)	Venter <i>et al.</i> (2007)
313	45.38 ± 0.84	43.99	42.05
323	32.29 ± 0.88	30.14	29.21
333	22.91 ± 0.83	22.17	20.93
343	17.54 ± 1.06	16.56	15.59
353	12.45 ± 0.35	13.02	12.14

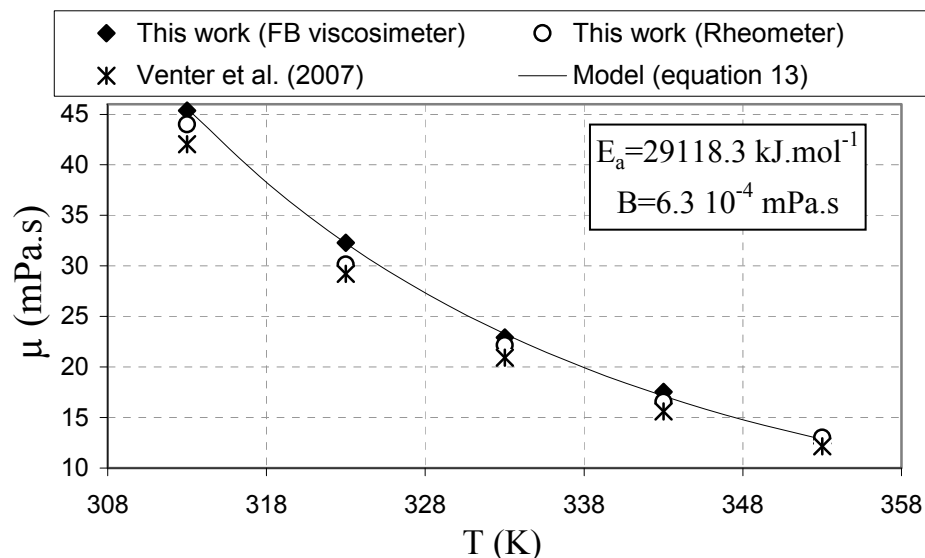


Figure 16. Viscosity measurements of cocoa butter as a function of temperature at atmospheric pressure

Viscosities of CO₂-saturated CB mixture were measured for pressures ranging from 0.1 to 25 MPa at 313.15 and 353.15 K. Our data were compared to those obtained by Venter *et al.* who performed measurements using a vibrating quartz viscometer (Table 8). Figure 17 and 18 show that our results are in agreement with literature data: MD is about 1.55 mPa.s at 313 K and 0.63 mPa.s at 353 K. From repeated measurements (at least three times for each data point)

with the FBV technique, a good precision was obtained (± 3 %) and a good reproducibility with Relative Standard Deviation (RSD) ranging between 0.3 and 2.9 %.

The viscosity decreases exponentially with the pressure. The magnitude of decreasing viscosity is about 93 % at 313.15 K and 85 % at 353.15 K. The maximal reduction is reached at approximately 15 MPa as observed by Venter *et al.* This tendency is attributed to the CO₂ dissolution into the melted media, which increases with the pressure as shown in Figure 18. From 15 MPa, the decrease of the viscosity slows down, so does the increase of the CO₂ solubility.

Table 8. Viscosity of cocoa butter saturated with CO₂ at 313 and 353 K

T (K)	P (MPa)	v (mm.s ⁻¹)	ρ_f (kg.m ⁻³)	μ_f (mPa.s)	RSD (%)	Re
313	0.10	0.39	894.97	45.38 ± 0.84	0.8	0.03
	4.23	0.97	902.88	18.12 ± 0.75	1.8	0.19
	8.45	2.04	909.89	8.62 ± 0.25	1.2	0.86
	10.60	4.15	911.25	4.20 ± 0.11	1.1	3.61
	15.90	4.87	920.10	3.58 ± 0.19	2.2	5.01
	19.93	5.42	925.12	3.21 ± 0.22	2.9	6.25
	25.22	5.54	930.93	3.14 ± 0.06	0.8	6.57
353	0.10	1.44	868.18	12.45 ± 0.35	1.3	0.40
	5.26	2.76	873.05	6.51 ± 0.16	1.0	1.48
	10.09	4.71	876.89	3.80 ± 0.15	1.7	4.35
	15.82	7.45	883.15	2.40 ± 0.03	0.5	10.98
	19.94	8.70	884.14	2.05 ± 0.02	0.4	15.03
	24.10	9.27	887.72	1.92 ± 0.03	0.3	17.14

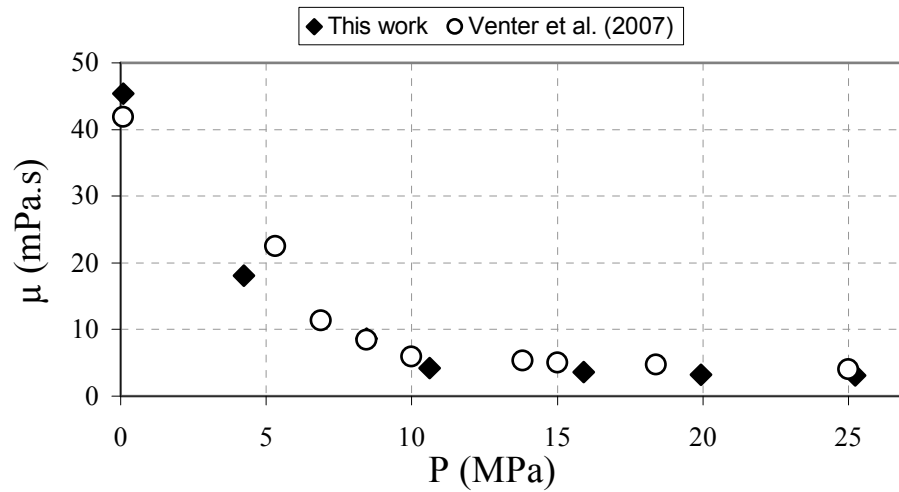


Figure 17. Viscosity measurements and literature data of cocoa butter saturated with CO₂ at 313 K

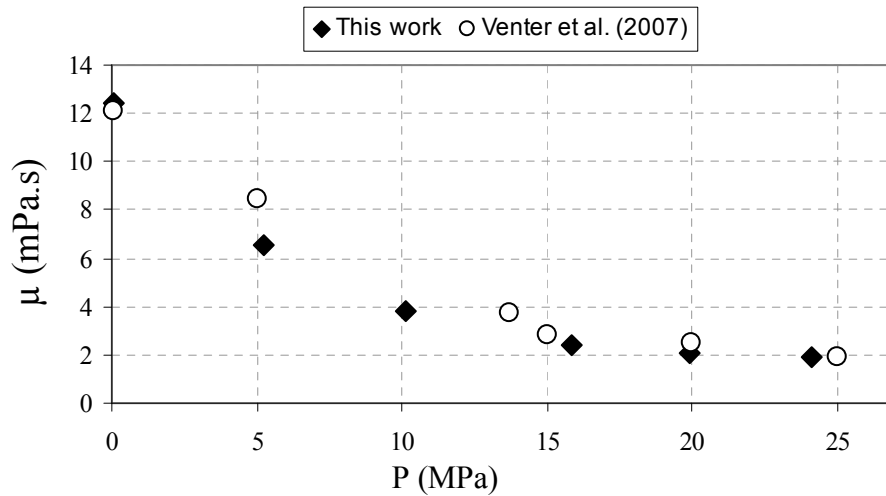


Figure 18. Viscosity measurements and literature data of cocoa butter saturated with CO₂ at 353 K

Several authors used models in order to correlate and predict the viscosity behaviour of lipids in contact with CO₂ (Kashulines *et al.*, 1991; Tuan *et al.*, 1999; Venter *et al.*, 2007). Tuan *et al.* compared the performance of the Ely and Hanley model, based on the corresponding states approach, and the Grunberg and Nissan model, which is an empirical model based on the modification of the Arrhenius equation (Grunberg and Nissan, 1949).

The first model is predictive and correlative. Yet, it requires the knowledge of viscosity, density correlations, critical properties, acentric factor and molecular mass for a reference fluid. It may be tricky to adapt to natural lipid mixtures. Thus, generally, empirical methods are used such as Grunberg and Nissan, particularly for binary mixtures containing polar components:

$$\ln \mu(T, P) = x_1 \ln \mu_1 + x_2 \ln \mu_2 + x_1 x_2 G_{12}(T) \quad (15)$$

where μ is the mixture viscosity at a given pressure and temperature and the indexes 1 and 2 correspond to the mixture components, respectively CO₂ and CB. μ_1 and μ_2 are the viscosities of the mixture components under the same conditions. Note that the pure CO₂ viscosities were taken from literature (Fenghour *et al.*, 1998). G_{12} is a binary parameter which is system-dependent and sometimes temperature-dependent (Mehrotra *et al.*, 1996). It allows taking into account the deviations from simple additive behaviour of the mixture viscosity (Irving, 1977). x_1 and x_2 are the mass fractions of the components in the CB-rich phase at a given pressure and temperature.

In the following, we consider that the mass fraction of CO₂ (x_1) is negligible compared to 1, the CO₂ viscosity is negligible compared to the CB one and the variation of CB viscosity with the pressure increase is low enough to be neglected. These assumptions lead to the following relation:

$$\ln \mu(T, P) = \ln \mu_{CB}(T, P_0) + x_{CO_2}(T, P) \cdot A_{12}(T) \quad (16)$$

where $\mu_{CB}(T, P_0)$ is determined by equation 13 and A_{12} is a binary parameter. The optimum value of G_{12} and A_{12} were determined using a curve fitting method with the Levenberg-Marquart algorithm. Results and performances of the two models are reported in table 9. Fitting curves of the two models are presented in the Figure 19.

Table 9. Parameters values and statistics of the viscosity correlation

Model	Parameters	AAD (%)	MaxD (%)	Bias (%)
Grunberg & Nissan	$G_{12} = -2.88$ (313 K) $G_{12} = -2.56$ (353 K)	14.9	35.6	5.9
Our Model	$A_{12} = -9.12$ (313 K) $A_{12} = -7.87$ (353 K)	11.4	24.7	2.4

Our model is slightly more accurate to represent the mixture viscosity according to the composition in CO₂ (AAD=11.4 %). Moreover, this model is simpler to use because it does not require the CO₂ viscosity. The maximum deviations for both models are observed for the highest CO₂ concentrations and are non-negligible. However, it turns out that the Bias value is lower for our model (2.4 %) which means that the distribution of the experimental points around the fitting curve is satisfactory. Hence, we can conclude that the model assumptions are valid for this kind of binary mixture.

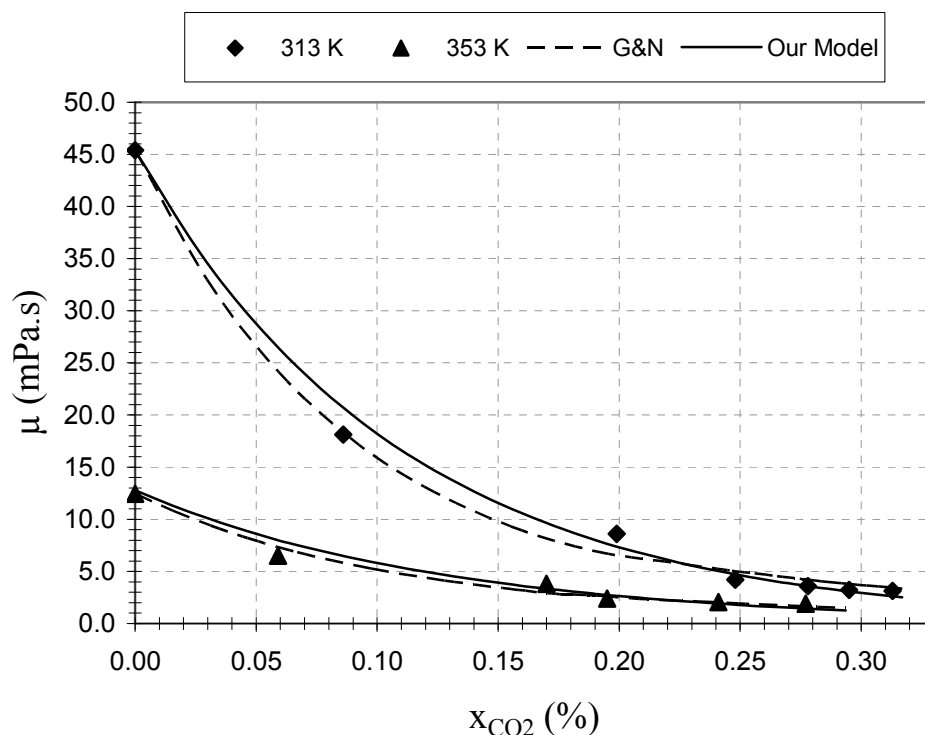


Figure 19. Viscosity of CO₂-saturated cocoa butter as a function of CO₂ solubility at 313 and 353 K

4. Conclusion

A set of physical properties of CO₂-saturated cocoa butter mixture have been measured, compared to literature data when available and modelled. These measurements were performed using characterization techniques that were set up and validated in a previous work. New reliable data on solubility, density,

volumetric expansion and viscosity have been produced which complement the literature. This data could be useful for designing future lipid applications.

In this work we have validated these techniques up to 35 MPa and 353 K; it appears that, within these limits, they are reliable and accurate. Comparison with literature for the CB-CO₂ mixture has been extensively studied: all the measurements are consistent with data already published for cocoa butter of the same origin.

This work provides new experimental data on the phase equilibrium behaviour of CB in contact with CO₂ such as the volumetric expansion and the inversion phase conditions. It is found that the solubility and density increase of CO₂ involves the phase inversion at 313 K and 40 MPa. Volumetric expansion is proportional to the quantity of dissolved CO₂, which varies linearly with pressure and is independent of temperature. This property may reach 47 %, and must therefore be known before designing a supercritical process, in particular for the equipment scale-up.

The density measurement method was found to be reliable ($\pm 0.60 \text{ kg}\cdot\text{m}^{-3}$). Its evolution with the CO₂ solubility is comparable to that of fish oil saturated with CO₂, which is mainly composed of polyunsaturated triglycerides. We modelled accurately the variations of density versus pressure and temperature with the modified Tait equation. Indeed, results obtained for density fitting are in good agreement with experimental data with an AAD of 0.044 %.

Our investigations with the falling ball viscometer show good reproducibility between the repeated measurements. This technique is a precision tool for viscosity measurements under high pressure ($\pm 3\%$). Viscosity data sets obtained both at atmospheric pressure and under high pressures are revealed to be in good agreement with the literature. We propose a new empirical relation, which correlates the viscosity of CO₂-CB mixture (with AAD=12.0 %) with the CB viscosity at atmospheric pressure and with its composition in CO₂.

Finally, the CO₂ solubility turns out to be the key property governing the evolution of all other properties. For instance, the dissolution of CO₂ causes a reduction in viscosity which can be as high as 90 %.

Notation

A	parameter in Equation (3)
B	parameter in Equation (3)
E	volumetric expansion in Equation (6), %
P	pressure, MPa
P ₀	atmospheric pressure, MPa
RSD	relative standard deviation

$$RSD = \frac{\sqrt{\frac{1}{N} \sum_{i=1}^{i=N} (x_i - \bar{x})^2}}{\bar{x}} \cdot 100$$

where x is the measurement and \bar{x} is the average between the repeated measurement.

T	temperature, K
V	volume at given pressure and temperature in Equation (6), ml
V_0	volume at atmospheric pressure and given temperature in Equation (6), ml
X_{CO_2}	solubility of CO ₂ in Equation (1), % (in mass)
x_{CO_2}	mass fraction of CO ₂ in Equation (13)

Greek letters

ρ	density, kg.m ⁻³
ρ_{cal}	calculated density in Equation (9), kg.m ⁻³
τ	oscillation period, s

Abbreviations

AAD	Absolute Average Deviation
Bias	Average deviation
CB	Cocoa Butter
CFD	Computational Fluid Dynamics
SC-CO ₂	Supercritical Carbon Dioxide
FBV	Falling Body Viscometer
MaxD	Maximum deviation
MD	Mean Deviation
VLE	Vapour-Liquid Equilibrium

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