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CHARACTERIZATION OF MELTED COCOA BUTTER SATURATED WITH SUPERCRITICAL CO₂

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Abstract. In this study, the measurements of density, solubility and volume expansion were carried out at 313 and 353 K and pressures of 5 to 25 MPa. The cocoa butter (CB) used in this work is manufactured by Gerkens Cacao. The experimental procedures were validated with the SC-CO₂/butan-1-ol mixture, for which literature data are available. In a first time, we focused on the density measurements, using the vibrating tube principle and on the solubility measurements of the SC-CO₂ in CB using a gravimetric procedure. We compared and discussed the results with literature data for instance with those of Venter *et al* [1], who performed density and solubility measurements using two different methods (gravimetric and static analytic methods). Phase composition and density measurements were carried out with a good reproducibility and repeatability. Moreover, the experimental density values were correlated with Tait and modified Tait equations and a model specially developed in this study. These models permitted to fit the experimental densities of pure CB and SC-CO₂/saturated CB mixture in a wide range of pressures and temperatures.

Key-words. Cocoa butter, supercritical CO₂, density, solubility, modelling, high pressure

1. INTRODUCTION

Supercritical fluid processes are emerging technologies as clean and efficient alternative to conventional methods in several fields such as extraction, crystallization, chromatography, material processing [2]. The supercritical carbon dioxide is commonly used and became the solvent of choice for food processing and pharmaceutical industries, because of its non toxicity and its moderate critical properties (critical pressure: 7.38 MPa, critical temperature: 304.35 K). In addition, the knowledge of vapour-liquid equilibrium (VLE) and volumetric properties as densities and viscosities of binary mixtures over an extended range of temperature and pressure are necessary for process design. Cocoa butter (CB) is used in the manufacturing of chocolate and may have other potential applications. It is a complex natural compound composed of different types of triglycerides (TG), which proportions vary according to the origin of the CB. This study is a preliminary work of a global project aiming at a new clean recrystallization / fractionation process of cocoa butter (CB) assisted by SC-CO₂. This process would be adapted to particle generation, which mean size, size distribution, polymorphism and lipid composition could be controlled. The fractionation of CB has not yet been fully explored but Bhaskar *et al.* [3] were the first to show that it was feasible. They used the difference of solubility in SC-CO₂ of the three most triglycerides contained in CB. This work as any other process design requires the knowledge of properties of the SC-CO₂ /CB system such as reciprocal solubility of the binary system, 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 thermophysical properties in the literature. In this work, we describe a new VLE measurements apparatus (static analytical method), equipped with U-tube densimeter for saturated densities measurements and a high precision balance for the gravimetric determination of phase compositions and its volume expansions. This study has been limited to the liquid phase composed of molten CB saturated in SC-CO₂.

2. MATERIALS AND METHODS

2.1. Materials

Cocoa butter was obtained from Gerkens Cacao (Wormer, The Netherlands) and was already used by Venter *et al.* Carbon dioxide (purity 99.995 %) was purchased from Air liquide S.A. (Paris, France). Butan-1-ol was purchased from Sigma-Aldrich. Pure water was obtained by ELGA purification system.

2.2. VLE Apparatus and procedure

A schematic diagram of the static analytical device for VLE and density measurements is shown in Fig. 1. The apparatus has been designed to carry out investigations under high pressure and high temperature, respectively up to 35 MPa and 473.15 K. The stainless steel autoclave (1), which capacity is 500 mL (Xenard, France), was previously loaded with 250 mL of melted cocoa butter 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 in the same pressure and temperature conditions than the autoclave, was used to maintain the equilibrium of the studied mixture. 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. Note the presence of a buffer storage tank (5) 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 5MPa above the equilibrium pressure in order to ensure a pressure drop compensation when valve V-9 was opened to make gravimetric analysis.

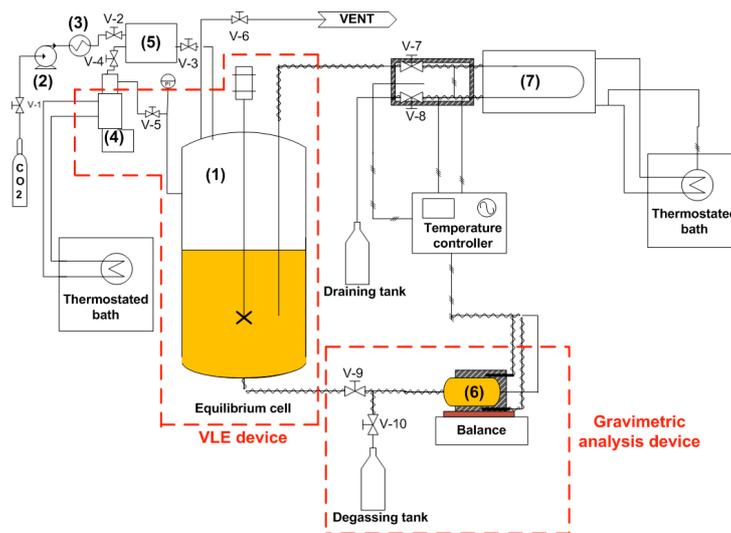


Fig. 1 Schematic diagram of the VLE apparatus

Then, the compensation operation was achieved by the membrane pump. The CO₂ flow compensation is fixed to $2 \text{ kg}\cdot\text{h}^{-1}$ in order to minimize the pressure drop ($\Delta P_{\text{max}}=0.5\text{MPa}$) manually controlled by V-7. Cell temperature was kept constant by means of PID controller within ± 0.1 K. This stainless steel measurement cell (Top-industrie, France) (6) was previously weighted empty and placed on a high precision balance (Sartorius Model LA3200B), was used to sample 50 mL of the liquid phase. This balance allows gravimetric analysis within ± 0.01 g. Moreover, density measurements were carried out in the same time with accuracy of $\pm 0.01 \text{ kg}\cdot\text{m}^{-3}$. Thus, valve V-7 is opened to refill the vibrating U-tube densimeter (Model Anton-Paar DMA-HPM) (7). Temperature in the vibrating U-tube is precisely controlled by a thermostated bath within ± 0.01 K and pressure is measured by a transducer (Model Druck PTX 611) with accuracy of ± 0.001 MPa. Volume within the loop remaining small, equilibrium is hardly perturbed and reached quickly. It is important to note that all pipes of the apparatus were precisely thermally controlled within ± 0.1 K. At last, when all parameters (pressure, temperature, mass) are stable, they were recorded and valve V-9 is closed to isolate the cell. The valve V-10 was then opened and the mixture is slowly degassed in order to recover cocoa butter and consequently to deduce the solubility of SC-CO₂ in the liquid phase. Then, for each experiment, the gravimetric analysis device was cleaned.

2.3. Validation of experimental procedure

The experimental procedure was validated comparing the results obtained from similar studies of the SC/CO₂-butan-1-ol system at 313.13 K [4-6] (Fig. 2).

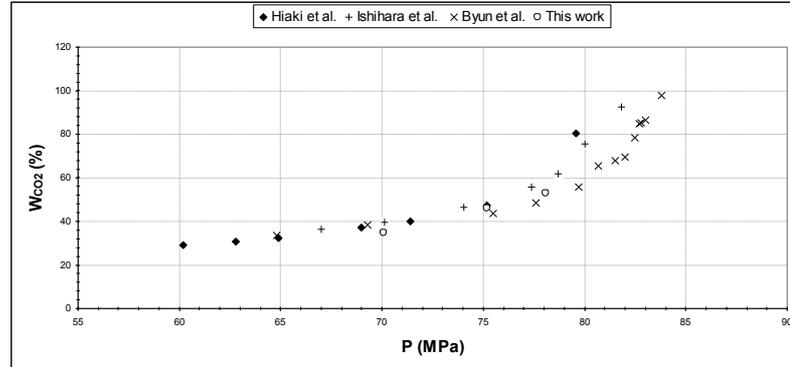


Fig. 2 Comparison of the measured and literature values for the liquid phase composition of SC-CO₂/butan-1-ol at 313.15K

In this work, the vibrating U-tube densimeter was calibrated with water and carbon dioxide 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 its mass (U-tube material and the fluid filling it). The behaviour of the vibrating tube can be compared to an undamped spring-mass, defined by its oscillation period, τ (s), such as:

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

where m_0 is the mass of the empty U-tube (kg), V is the volume of the tube (m³), ρ is the density of the fluid (kg.m⁻³) and D is the spring constant (N.m⁻¹). Rearrangement of this equation leads to a simple definition of the density commonly used in the vibrating tube technology, like:

$$\rho = A\tau^2 - B$$

The apparatus parameters A and B are defined from measured oscillation periods at fixed pressure and temperature conditions and known densities of water [7] and carbon dioxide [8], such as:

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

It is important to note that 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, it gives a quite good stability to the thermodynamic equilibrium and to the density measurements. Each experimental point was performed at least three times. The average value is given with a relative mean deviation of 0.06 %, whatever experimental conditions are. For instance, at 25 MPa and 313.15 K, density equals to 931.48 ± 0.56 kg.m⁻³.

3. RESULTS AND DISCUSSION

3.1. Density measurements and modelling

Densities were measured for CB and SC-CO₂-saturated CB mixture for pressure ranging from 0.1 to 25 MPa and at 313.15, 323.15 and 353.15 K. The density of CB decreases linearly with the temperature at constant pressure and conversely the density increases linearly with the pressure at constant temperature (Fig. 3(a), 3(b)). The same behaviour for the density of CB-CO₂ is observed (Fig. 3(a), 3(c)) and thus the increase of density depends only on the increase of CO₂ pressure. However, the magnitude of increase in density is relatively small and decreases with temperature.

This behaviour can be attributed to the decrease of the mixture compressibility with the temperature, which is defined as:

$$\chi = \frac{1}{V} \cdot \left(\frac{\partial V}{\partial P} \right)_T$$

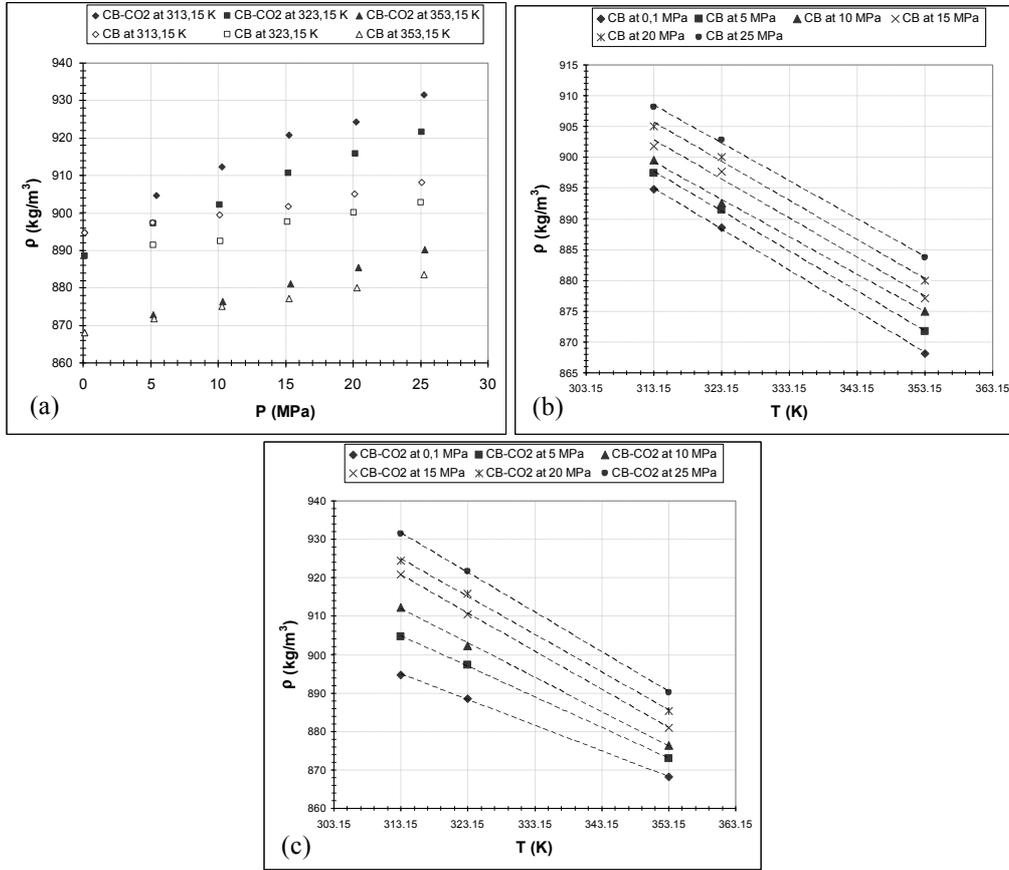


Fig. 3 CB and CB-CO₂ density dependence of the pressure (a) and the temperature (b, c)

The variations of density versus pressure and temperature can be represented for CB and the CO₂-saturated CB mixture by three empirical models:

- Tait equation [9]:

$$\rho(T, P) = \frac{\rho(T, P_0)}{1 - C \ln\left(\frac{B(T) + P}{B(T) + P_0}\right)} \quad \text{with} \quad B(T) = B_0 + B_1 \cdot T + B_2 \cdot T^2$$

- Modified Tait equation [9]:

$$\rho(T, P) = \frac{\rho(T, P_0)}{\left(1 - \frac{A \cdot P}{\Pi + P}\right)} \quad \text{with} \quad \Pi(T) = \Pi_0 + \Pi_1 \cdot T + \Pi_2 \cdot T^2$$

- Our empirical equation:

$$\rho(T, P) = \rho(T, P_0) \cdot (1 + (P - P_0) \cdot \chi(T)) \quad \text{with} \quad \chi(T) = \chi_0 + \chi_1 \cdot T + \chi_2 \cdot T^2$$

This last model was proposed in this study and compared with Tait equations, which are widely used to fit high pressure density of solids, dense gases, pure liquids and mixtures. Note that B(T), C, A and $\Pi(T)$ are fitting parameters without physical meaning for Tait equations on the contrary of $\chi(T)$, which corresponds to the fluid compressibility depending on temperature for our equation. Indeed, this last physical parameter is only dependent on temperature considering that the molten CB is incompressible.

The density of the fluid at the reference pressure ($P_0=0.1$ MPa) is depending on temperature as:

$$\rho(T, P_0) = \rho_0 + \rho_1 \cdot T$$

Thus, CB and SC-CO₂-saturated CB mixture densities values at 313.15, 323.15 and 353.15 K were fitted by these three models. In order to evaluate and compare the performance of these models, we introduce the characteristic quantities as:

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

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 (MD) characterizes the maximum deviation generated by the model. In this work, we programmed the Levenberg-Marquardt algorithm [10] under Matlab[®]. It is a very useful method for non-linear squares problem, allowing in our case to determine the optimal combination of fitting parameters of Tait and modified Tait equations in order to minimize the deviation in relation to the experimental data.

Table 1 Fitting parameters and characteristics quantities for the density modelling

Fluid	Tait Equation	Modified Tait Equation	Our Equation
SC-CO ₂ / CB	A=0.12410	C=0.05050	$\rho_i=1104.30$
	$\Pi_i=1969.40419$	$B_i=791.54960$	$\rho_i=-0.67$
	$\Pi_i=-12.73093$	$B_i=-5.11247$	$\chi_i=1.07693 \times 10^{-2}$
	$\Pi_i=0.02114$	$B_i=0.00847$	$\chi_i=-3.48272 \times 10^{-5}$
	AAD=0.067 %	AAD=0.044 %	$\chi_i=2.01905 \times 10^{-8}$
	MD=0.176 %	MD=0.180 %	AAD=0.124 %
	Bias= 1.24×10^{-2} %	Bias= 1.03×10^{-2} %	MD=0.540 %
			Bias= 5.73×10^{-3} %
CB	A=60.8408	C=11.6688	$\rho_i=1104.30$
	$\Pi_i=4.05946 \times 10^6$	$B_i=7.74510 \times 10^5$	$\rho_i=-0.67$
	$\Pi_i=-2.33272 \times 10^4$	$B_i=-4.44877 \times 10^3$	$\chi_i=-4.29328 \times 10^{-3}$
	$\Pi_i=34.21950$	$B_i=6.52325$	$\chi_i=2.56588 \times 10^{-5}$
	AAD=0.044 %	AAD=0.044 %	$\chi_i=-3.24049 \times 10^{-8}$
	MD=0.177 %	MD=0.174 %	AAD=0.061 %
	Bias= 4.69×10^{-3} %	Bias= 2.76×10^{-3} %	MD=0.141 %
			Bias= 3.36×10^{-3} %

Results obtained for density fitting show that the best ones in terms of AAD for SC-CO₂ / CB mixture and pure CB are obtained with the modified Tait equation, for which AAD is only 0.044 %. Nevertheless, results obtained with our model are satisfactory and specially the distribution of experimental points around the fitting curve is better than other models with the lowest Bias. Moreover, our equation is easier to use because it is not necessary to use optimization methods as Levenberg-Marquart algorithm for the determination of parameters.

3.2. Solubility of CO₂ in cocoa butter

The phase behaviour of SC-CO₂ / CB system was already studied by means of a view cell to observe the formation of a third phase or a phase inversion [1]. It appeared that nothing occurred between 313 K and 363 K and pressures up to 35 MPa, which seems consistent with other literature results: the studied experimental domain is not large enough to reach the equidensity pressure defined as the pressure giving the same density for both phases. Hence, at 313.15 K, by assuming that the vapour phase density corresponds to that of pure SC-CO₂ because of the phase composition, which reaches 98 to 99 % of CO₂ according to Kokot *et al.* [11], the equidensity pressure of the liquid and vapour phase is calculated and estimated to be 38 MPa. This estimation is obtained by comparing the variations of SC-CO₂-saturated CB mixture (modelled by modified Tait equation) and pure CO₂ densities versus pressure. Yet, we have experimentally observed the phase inversion at 307.15 K. It can be observed that the surface tension of the melted phase decreases with the pressure and thus with the increase of SC-CO₂ solubility until the vapour phase forms a bubble surrounded by the melted phase. Consequently, at 307.15 K, the equidensity pressure is found to be 33 MPa compared to 33.5 MPa for the calculated one. In this work, the solubility of SC-CO₂ is defined as a mass percentage of CO₂ contained in the liquid phase rich in melted cocoa butter and permits to deduce volume expansion, such as:

$$\Delta V = \frac{V_{\text{mixture}} - V_{CB}}{V_{\text{mixture}}} \cdot 100 = \frac{\frac{m_{\text{mixture}}}{\rho_{\text{mixture}}} - \frac{m_{CB}}{\rho_{CB}}}{\frac{m_{\text{mixture}}}{\rho_{\text{mixture}}}} \cdot 100$$

where m_{CB} is the mass of cocoa butter (g), obtained after the depressurization of the cell measurement and degassing operation allowing to determine the mass of CO_2 dissolved in the liquid phase sample.

Fig. 4(a) show that the solubility of CO_2 increases with the pressure and decreases with the temperature as it has been observed in literature [1, 11]. In addition, we can see that our results are in good agreements with those of Venter *et al.* [1]. Relative mean deviations on measurements of CO_2 solubility are respectively 1.4 % and 3.6 % at 313.15 K and 353.15 K, whatever pressure conditions. At 313.15 K, CO_2 solubility reaches a maximum of 31.3 ± 0.5 % and causes a volume expansion of 42 % of the melted phase.

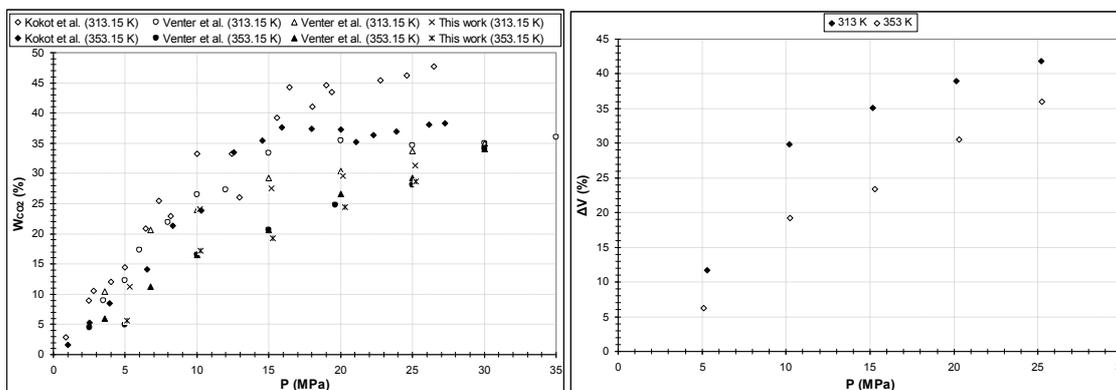


Fig. 4 CO_2 solubility (a) and volume expansion (b) of the liquid phase at 313.15 K and 353.15 K

4. CONCLUSION

A new static analytical device, easy to set up and to handle has been developed. It can be used to carry out VLE experiments with a good reproducibility and repeatability of density and phase composition measurements. These results have been compared with literature and are found to be in good agreement with those of Venter *et al.* [1]. A new model based on compressibility has been proposed to fit the experimental density of pure fluid and binary mixture in a wide range of pressures and temperatures.

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