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Phase equilibria and physical properties of CO_2-saturated cocoa butter mixtures at elevated pressures

M.J. Venter [a,*,1], P. Willems [a,1], S. Kareth [b,2], E. Weidner [b,2], N.J.M. Kuipers [a,1], A.B. de Haan [c,1]

[a] *Separation Technology Group, Faculty of Science and Technology, University of Twente, P.O. Box 217, 2500 AE Enschede, The Netherlands*
[b] *Chair of Process Technology, Ruhruniversity Bochum, Universitätstr. 150, 44780 Bochum, Gebäude IB 6/126, Germany*
[c] *Eindhoven University of Technology, Department of Chemical Engineering and Chemistry, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*

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Abstract

The melting point and phase behaviour of cocoa butter under CO_2 pressure were observed in a high-pressure view cell. The melting point decreases from 35 to 23 °C at CO_2 pressures higher than 5 MPa. A static analytical procedure was used to measure the solubility of CO_2 in cocoa butter at 40, 80 and 100 °C and pressures of 2–35 MPa in an autoclave set-up. The density and viscosity of the CO_2-saturated cocoa butter was measured simultaneously in this set-up. The experimental procedure was first validated by comparing the data measured for the system CO_2/hexadecane with literature data. The highest solubility of CO_2 in cocoa butter of 36 wt.% occurs at 40 °C and 35 MPa. The measured solubilities differed from those previously reported in literature. This can be attributed to differences in the cocoa butter used for measurements. The density of CO_2-saturated cocoa butter increases with pressure, whereas the viscosity decreases. The Grunberg equation was used to correlate the viscosity of CO_2-saturated cocoa butter. The measured data were used to estimate the theoretical gas assisted mechanical expression (GAME) yields. In GAME CO_2-saturated cocoa nibs are mechanically expressed. The calculated GAME yields deviate from the experimental ones due to the oversimplification of the mechanism involved in GAME.

Keywords: Cocoa butter; Density; Gas assisted mechanical expression; High-pressure phase equilibrium; Supercritical carbon dioxide; Viscosity

1. Introduction

Cocoa butter is used in the manufacturing of chocolate, making it one of the most important ingredients used by the confectionery industry [1]. Since 1828, when Van Houten developed a press to produce partially defattened cocoa beans [2], mechanical pressing has been used to generate good quality cocoa butter from cocoa beans. However, mechanical pressing can only remove a limited amount of cocoa butter from the cocoa beans [2–4]. Recently a new process, gas assisted mechanical expression (GAME), has been proposed as an improved method for obtaining good quality cocoa butter from cocoa beans at high yields [4]. In this process supercritical carbon dioxide (SC-CO_2) saturated cocoa nibs are mechanically pressed. In GAME the high solubility of SC-CO_2 in cocoa butter is used to increase the cocoa butter yield that can be obtained with mechanical pressing. This is in contrast to supercritical extraction, where the solubility of the cocoa butter in SC-CO_2 is the important parameter. Data on the solubility of SC-CO_2 in cocoa butter, as well as on the viscosity and density of SC-CO_2-saturated cocoa butter are needed for the characterisation and design of a GAME process. The GAME cocoa butter yields can be predicted from the yield obtainable with conventional expression at the same effective mechanical pressure when the CO_2-content and density of the CO_2-saturated cocoa butter are known.

Limited information on the properties of SC-CO_2-saturated cocoa butter could be found in literature. Kokot et al. [5] investigated the melting point of SC-CO_2-saturated cocoa butter as well as the solubility of SC-CO_2 in cocoa butter at 30, 40, 60 and 80 °C. This data was previously used to predict GAME yields

* Corresponding author. Fax: +31 53 489 4821.
E-mail address: daleenventer@gmail.com (M.J. Venter).
[1] Fax: +31 53 489 4821.
[2] Fax: +49 234 321 4277.

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from conventional expression yields with a reasonable accuracy [4]. However, no data could be found for the density and the viscosity of SC-CO_2-saturated cocoa butter or the properties of SC-CO_2-saturated cocoa butter at 100 °C.

In this work a new experimental set-up consisting of an autoclave fitted with a magnetically coupled stirrer, an inline quartz viscosimeter and an external density sensor was developed to simultaneously measure the CO_2-content, density and viscosity of CO_2-saturated cocoa butter at 40, 80 and 100 °C and pressures of 2–35 MPa. This set-up allows equilibrium to be reached at shorter times (∼5 min) than those necessary for shaken autoclaves (∼30 min) like the one used in [5]. Cocoa butter was considered as a single compound for the purposes of this study, following the example of others who measured phase equilibria of SC-CO_2/plant oils [5–9]. The experimental procedure was first validated by comparing the measured CO_2 solubility in *n*-hexadecane as well as the viscosity of CO_2-saturated *n*-hexadecane at 40 and 60 °C and pressures of 2–22 MPa with literature values. *n*-Hexadecane was used as a test compound as it is a non-volatile organic compound, and can therefore be expected to behave in a similar way as cocoa butter. The ability to reproduce literature data was used as a proof of acceptable experimental procedure and analysis. The melting point depression of cocoa butter in the presence of SC-CO_2 was investigated in a high-pressure view cell. Qualitative observations of the phase behaviour of cocoa butter/CO_2 were also made with the view cell.

2. Materials and methods

2.1. Experimental set-up and procedure

2.1.1. Equipment

2.1.1.1. View cell. A high-pressure cell with a total interior volume of 25 cm^3 was used for qualitative phase behaviour observations. This cell contains two glass sight windows and can withstand pressures of up to 20 MPa. A heating jacket allows operation at a constant temperature ± 0.5 °C. The temperature is measured with a thermocouple fitted to the upper third of the cell. A magnetic stirrer enables mixing of the substances inside the view cell.

2.1.1.2. Static analytic set-up. Details of the static analytic set-up used for phase equilibrium, density and viscosity measurements are shown in Fig. 1. The apparatus consists of a 500 ml autoclave (10) fitted with a quartz viscosimeter (3) allowing continuous viscosity measurement (QVis 01/o, Flucon, Clausthal-Zellerfeld, Germany) and a magnetically coupled stirrer (7) (Cyclone 075, Büchiglasuster, Uster, Switzerland). The pressure was measured with a pressure transducer (PTX7517, maximum pressure 70 MPa, accuracy ± 5% full scale, Druck Nederland, Barendrecht, The Netherlands). Teflon seal rings were used to ensure a gas-tight set-up. A dip tube (5) enables sampling of the heavy phase inside the autoclave. The sampling line is connected to an external oscillating density meter (8) (DMA 512P, Anton Paar, Graz, Austria). The temperature of the set-up is kept constant within ± 1 °C by circulating thermal

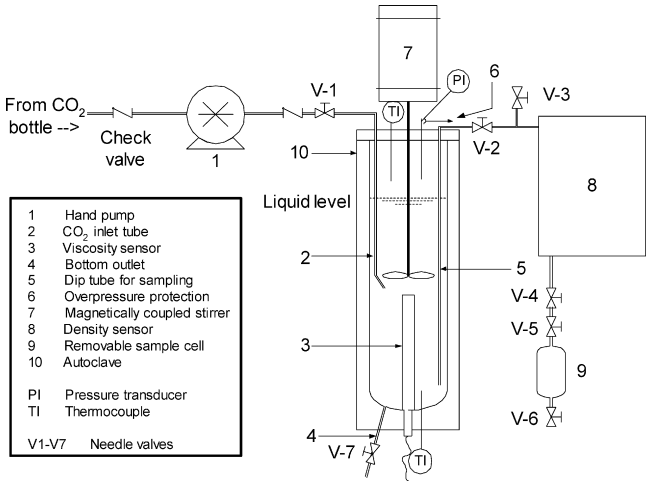

Fig. 1. Schematic diagram of the autoclave set-up.

oil through the jackets of the autoclave and density sensor. A removable sample cell (9) is connected to the density sensor. The system can withstand pressures up to 45 MPa and temperatures up to 120 °C. A relief valve is connected to the autoclave to protect the system against overpressures. A bursting disk is also present in case the relief valve malfunctions.

2.1.2. Procedures

2.1.2.1. Melting points. The melting points of pure and CO_2-saturated cocoa butter were visually observed with the view cell set-up by loading the cell with a small amount of cocoa butter and slowly increasing the temperature with and without CO_2 present. It is expected that the melting point found in this way will not differ from the solidification temperature measured by decreasing the temperature, since cocoa butter does not display hysteresis [5].

2.1.2.2. Phase equilibrium, density and viscosity measurements. The density sensor in the autoclave set-up was calibrated with air and *n*-hexadecane. The calibration of the viscosity sensor in this set-up was checked with the atmospheric cocoa butter viscosity data measured at different temperatures. The atmospheric viscosity of the cocoa butter at temperatures of 35–90 °C was measured with an Ubelohde viscometer (capillary diameter 1.13 mm) purchased from Schott (Mainz, Germany) placed in a constant temperature bath (set point ± 0.1 °C). The atmospheric density of the cocoa butter at temperatures of 35–90 °C was measured with an oscillating densimeter (DMA5000, Anton Paar, Graz, Austria).

The numbers in this paragraph refer to the numbers shown in Fig. 1. The autoclave (10) was loaded with 200–300 ml of test compound and allowed to reach the desired temperature before CO_2 from the supply cylinder was added with a hand pump (1) (Sitec Hand Pump 750.1060, Sitec Sieber Engineering, Zürich, Switzerland), of which the fluid chamber is cooled to 10 ± 1 °C. In all cases the CO_2 had to diffuse into the unsaturated liquid. The mixture in the autoclave was stirred at 500 rpm for at least 5 min to ensure that phase equilibrium has been reached. Letourneau