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Melting point depression of solid lipids in pressurized carbon dioxide

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ABSTRACT

Understanding the melting behavior of solid lipids in pressurized carbon dioxide (CO_2) is important for the production of solid lipid particles using supercritical CO_2. Melting point depression and volumetric expansion of solid lipids in pressurized CO_2 was studied as a function of pressure. The highest melting point depression (76.5%) was observed for coconut oil at 43 bar, whereas the lowest was for fully hydrogenated canola oil (18.5%) at 122 bar. The lipids composed of shorter chain fatty acids exhibited higher melting point depression. A positive correlation was observed between the melting point depression and volumetric expansion of the lipids. The lowest expansion was observed for fully hydrogenated canola oil (9.7%), whereas the highest was for lauric acid (42.7%) at the lowest pressure where the lipids melted. Supercritical CO_2 technology can lead to energy savings in particle formation processes due to lower melting temperatures and also provide better protection of the bioactives in such potential delivery systems.

1. Introduction

There is growing interest in supercritical carbon dioxide (SC-CO_2) technology as a 'green' technology for the processing of materials in the food, pharmaceutical and chemical industries due to its well-known advantages. The application of supercritical fluids for particle design to deliver pharmaceutical and bioactive substances has attracted great attention and several new particle formation methods based on supercritical fluid technology have been developed [1]. Among them, lipid-based particle formation using SC-CO_2 is of particular interest. Continuous development of know-how in the supercritical fluid processing of fats and oils has led to new application areas and advanced methods [2].

Development of solid lipid particles is one of the emerging fields of particle formation with several potential applications in drug delivery and clinical medicine as well as the delivery of bioactives in functional food products. Generally, lipid particles are produced first by melting the solid lipid and bioactive mixture, then homogenizing the mixture and finally solidifying by cooling [3]. Temperature is a key parameter for lipid particle production. Processing temperature must be high enough to keep the solid lipid mixture in liquid state during homogenization. However, high temperature melt processing limits the use of several bioactive compounds due to their thermally-labile nature.

SC-CO_2 process also has the potential to overcome the problems associated with the high melting temperature of solid lipids during the particle formation processes by decreasing the melting temperature of the solid lipid. Investigation of the melting behavior is essential for designing supercritical processes for lipid particles production. Generation of melting curves provides useful information that would allow us to know at what pressure and temperature the solid lipid would melt.

Melting point depression in supercritical fluids has been demonstrated in the literature for semi-crystalline polymers [4,5], drug molecules [6,7] and β-sitosterol [8]. However, the literature on the melting behavior of solid lipids is scarce. Kokot et al. [9] and Venter et al. [10] determined the melting point of cocoa butter in CO_2 using a modified capillary method in a high pressure optical cell and in a thermostated view cell, respectively. Sousa et al. [11] investigated the melting behavior of lipid matrices in CO_2 using a modified capillary method similar to that of Kokot et al. [9]. Spilimbergo et al. [12] used a high pressure differential scanning calorimeter to study the effects of CO_2, chlorodifluoromethane and 1,1,1,2-tetrafluoroethane on the melting point of pure tristearin and tristearin–phosphatidylcholine–dioctyl sulfosuccinate mixture only up to 60 bar because the maximum operating pressure of the instrument was 70 bar. In another study, Li et al. [13] studied the binary solid–liquid–gas (S–L–G) equilibrium of the tripalmitin/CO_2 system.

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Table 1
Fatty acid composition and melting point of the lipids, and the points on the melting curves (Points A and B in Fig. 2) where volumetric expansion of the lipids in pressurized CO_2 was studied.

Lipid	Main fatty acids of the lipid (%)	Melting point at atmospheric pressure (°C)	Point A T (°C)/P (bar)	Point B T (°C)/P (bar)
Tristearin		73.0	62.3/149	62.3/243
Monostearin		70.0	51.7/96	52.0/176
Stearic acid		69.0	58.2/133	58.3/224
Trilaurin		46.5	30.0/80	30.0/214
Lauric acid		46.0	26.8/67	28.0/274
Fully hydrogenated canola oil	$C_{16:0}$: 5.0 $C_{18:0}$: 88.2 $C_{18:1}$: 3.3	71.5	58.3/122	58.3/211
Cocoa butter	$C_{16:0}$: 29.8 $C_{18:0}$: 33.3 $C_{18:1}$: 31.8	32.0	21.1/60	21.0/198
Coconut oil	$C_{8:0}$: 8.0 $C_{10:0}$: 6.5 $C_{12:0}$: 50.1 $C_{14:0}$: 18.6 $C_{16:0}$: 8.3 $C_{18:0}$: 2.9 $C_{18:1}$: 4.8	34.0	8.0/43	8.0/200

It is evident that the literature lacks information on the melting behavior of solid lipids saturated with CO_2 under high pressure but this fundamental information is essential for developing novel processes to generate lipid particles. Therefore, the objective of this study was to investigate the melting behavior of pure lipids of different classes (tristearin, trilaurin, monostearin, stearic acid and lauric acid) and complex mixtures of real samples (fully hydrogenated canola oil, cocoa butter and coconut oil) after saturating them with CO_2 at pressures of up to 350 bar in a high pressure view cell using a modified "first melting point" method.

2. Materials and methods

2.1. Materials

Unrefined coconut oil and cocoa butter were purchased from a local market. Fully hydrogenated canola oil was kindly provided by Richardson Oilseed Ltd. (Lethbridge, AB, Canada). Tristearin (≥80%), trilaurin (≥98%), monostearin (≥60%), stearic acid (≥95%) and lauric acid (≥98%) were purchased from TCI America (Portland, OR, USA). Melting points of these lipid samples determined in this study at atmospheric pressure are given in Table 1. All of the pure lipids were in crystalline powder form. Fatty acid methyl ester standards were purchased from Nu-Chek Prep Inc. (Elysian, MN, USA). CO_2 (99.8% bone dry, water level <3 ppm) was obtained from Praxair Canada Inc. (Mississauga, ON, Canada).

2.2. Determination of fatty acid composition

Fatty acid composition of the coconut oil, cocoa butter and fully hydrogenated canola oil were determined using a gas chromatograph (Varian 3400, Varian Inc., Walnut Creek, CA, USA) equipped with a flame ionization detector. Lipid samples were methylated and dissolved in hexane (0.4 mg/mL) prior to analysis by gas chromatography as described previously [14]. Fatty acids were identified by comparison of the retention times with those of authentic standards and the results are reported as the area percentage of the peaks.

2.3. Melting point measurements in pressurized CO_2

Melting point measurements of the lipid samples saturated with CO_2 were carried out using a phase equilibria apparatus (SITEC-Sieber Engineering AG, Maur/Zurich, Switzerland) (Fig. 1). The temperature of the cell was maintained at 5 °C above the melting point of the lipid sample by circulating water:ethylene glycol mixture (50:50, v:v) using a refrigerated circulator (model 1162A, VWR Inc., Radnor, PA, USA). Lipids were melted in an oven at 80 °C to erase the crystal memory, and 100 μL of molten fat was loaded into a transparent glass gas chromatography vial insert (200 μL, 6 × 28 mm) placed in a transparent 2 mL vial. The vial was then placed into the high pressure vessel at a position where the sample could be seen by the camera through the sapphire window, and then the cap of the vessel was closed. The lipid was kept in the vessel for 10 min to attain thermal equilibrium. The sampling valve of the vessel was opened, and the vessel was gently purged with CO_2 to remove any residual air. Then, the sampling valve was closed, and the vessel was filled with CO_2 using a syringe pump (Model 250D, Teledyne Isco Inc., Lincoln, NE, USA) until the desired pressure was reached. The system was equilibrated for 1.5 h by keeping the system at the set pressure and temperature. Then, the vessel was cooled down using the refrigerated circulator until the solidification of the CO_2-saturated lipid was observed. Phase change of the lipids was visually observed on the computer screen via the real-time image captured by the microscope and the camera placed in front of the sapphire window when the image became dark. Upon solidification of the sample, the temperature of the cell was decreased to 5 °C below the observed solidification temperature, and maintained constant at this temperature for 10 min. Then, the temperature of the vessel was increased to the melting temperature of the CO_2-saturated lipid at a heating rate of 1.3 °C/min. The melting temperature and pressure of the CO_2-saturated lipid was recorded as the pressure and temperature at which the first brightness in the picture of the lipid sample during the heating step was observed. It was not possible to observe complete melting of the sample because the bottom of the sample was below the level of the sapphire window. Melting point depression was calculated as follows:

$$\text{Melting point depression}\,(\%) = \left(\frac{\text{MP}_i - \text{MP}_p}{\text{MP}_i}\right) \times 100 \quad (1)$$

where MP_i is the initial melting point of lipid under atmospheric conditions and MP_p is the melting point of CO_2-saturated lipid under pressure.