Thermochimica Acta 549 (2012) 116–123

Contents lists available at SciVerse ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Thermal characteristics of freeze-dried camel milk and its major components

Mohammad Shafiur Rahman*, Halaa Al-Hakmani, Ahmed Al-Alawi, Insaaf Al-Marhubi

Department of Food Science and Nutrition, Sultan Qaboos University, P.O. Box 34, Al-Khod 123, Oman

ARTICLE INFO

Article history:
Received 26 May 2012
Received in revised form 30 August 2012
Accepted 8 September 2012
Available online 17 September 2012

Keywords:
Melting
Glass transition
Camel milk
State diagram
Whey
Casein
Lactose

ABSTRACT

Thermal characteristics of freeze-dried whole and skimmed camel milk, and its major components were measured by differential scanning calorimetry (DSC). The thermogram of whole milk showed three endothermic peaks (two for fat-melting and the other for non-fat solids-melting) and three shifts. Two shifts at low temperature were related to the glass transitions. The shift at higher temperature after melting of non-fat solids could be related to the structure ordering in milk after solids-melting. It was difficult to identify which components in the milk were providing these transitions and to trace the glass transitions of each component in the milk due to the complex interactions of the components' phases. For this reason, different major components of the camel milk (fat, cream, casein, whey protein, and lactose) were separated and then measured its thermal characteristics. The thermogram of camel milk fat showed two endothermic peaks, one wide and the other sharp. The shape of the endotherm for fat was related to the melting of different fractions of fatty acid. The glass transitions of the isolated casein, whey and lactose were also determined separately.

1. Introduction

Milk is a natural healthy food for children and adults. It is a complex mixture containing carbohydrate (mainly lactose), fat, protein, essential minerals (like calcium, phosphorous and others) and vitamins. Human consumes milk from different animals, such as cow, goat and camel. Milk is consumed as a beverage, and used to make butter, cream, yogurt, cheese, and a variety of other products, such as milk powder when milk production increased.

Besides the common nutritional value of milk, camel milk showed nutritional and interesting therapeutic properties. It contained appreciable amounts of essential fatty acids and contained higher amount of antimicrobial agents as compared with other sources of milk [1]. The main components of whey proteins in camel milk and colostrum were similar to that in bovine, except for the lack in β-lactoglobulin. Camel milk and colostrum were shown to be rich in protective proteins, especially immunoglobulin (IgG_2 and IgG_3), which revealed to be a potential source of inhibitory antibiotics [2]. Camel milk antimicrobial agents were more heat resistant than cow and buffalo milk proteins [3,4]. Chemical composition, fatty acid and protein profiles of camel milk were studied earlier in order to determine its nutritional value [2,5–8]. Zhang et al. [9] studied the changes in chemical composition of camel milk during lactation. Antoine and De Souza [10] studied the denaturation temperature of cow milk whey protein mainly containing β-lactoglobulin, α-lactalbumin, and serum albumin as a function of pH. Camel milk whey protein exhibited markedly lower sensitivity to heat denaturation as compared to cow milk whey protein [11].

Thermal characteristics, such as glass transition, melting and freezing point of foods are important in determining its stability during processing and storage [12,13]. The quality of milk powder deteriorated by fat oxidation [14], non-enzymatic browning [15], stickiness, caking, collapse and sugar crystallization [16–21]. Glass transition of milk and its components were affected by storage. The stability of protein [22], lactose crystallization [23–25], and dairy products [26] were reported earlier. It is important to know the melting point of fat since milk storage above melting could initiate undesirable agglomeration and caking [27].

In most of the cases in the literature, thermal characteristics of whole foods or food ingredients were measured. However, negligible work was presented by measuring thermal characteristics of foods and its extracted or separated components as well. Milk is a multicomponent mixture containing mainly water, protein, fat, lactose and other minor constituents, thus it is a challenge to trace different state and phase changes from its complex thermogram as measured by differential scanning calorimetry (DSC). Negligible research works were reported on the thermal characteristics of camel milk powder, especially for its major components. The objectives of this study were to determine the thermal characteristics of whole and skimmed camel milk; and its isolated components (i.e. fat, cream, casein, whey protein and lactose) using differential scanning calorimetry (DSC). These thermal characteristics data could be used in determining the storage stability of dried camel milk.

* Corresponding author. Tel.: +968 24141273; fax: +968 24413418.
E-mail address: shafiur@squ.edu.om (M.S. Rahman).

0040-6031/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.tca.2012.09.005

2. Materials and methods

2.1. Materials

One batch of pasteurized (60 °C, 30 min) whole camel (local breeds were selected random on a normal diet) milk was provided by Royal Court Affairs (Barka, Oman). The samples were immediately cooled at 4 °C and transferred to the laboratory within 12 h, and kept frozen at −40 °C until used for experiments. Commercial lactose (D-lactose monohydrate) was purchased from VWR International, Poole, England.

2.2. Preparation of cream

The cream was prepared similar to Karray et al. [28] with some modification. Four hundred milliliters of pasteurized whole camel milk was centrifuged at 5000 × *g* for 30 min at 4 °C. The top layer (cream) was separated manually from the supernatant and divided into two equal halves; one half was freeze-dried and the other half was set aside for fat analysis. The supernatant was used as skimmed milk.

2.3. Separation of milk fat

Milk fat was separated using Rose-Gottlieb method described by Ronald and Ronald [29]. The procedure involved placing 12 g of milk cream in a Mojonnier extraction flask along with 10 ml distilled water (50 °C) and 2.5 ml ammonia solution and mixed by gentle swirling. Then, two drops of phenolphthalein indicator, 10 ml of ethanol, and 25 ml diethyl ether were added to the mixture. The mixture contents were shaken and buildup gases were released repeatedly; and 25 ml of petroleum ether was added to the mixture. The new mixture was shaken; buildup gases were released and then allowed to stand for 20 min (until the supernatant layer was distinctly separated from the aqueous layer). The upper layer (solvent layer) was carefully collected and extraction step was repeated twice. Finally, the combined solvent was left in a fume hood to evaporate for 24 h, and further dried in air oven for 2 h at 100 °C.

2.4. Preparation of casein protein

The preparation of casein protein was as follows: 20 ml of 10% acetic acid (v/v) was added to the 400 ml of defatted skimmed milk and then allowed to stand for 30 min at 35 °C. Solution of 1 M sodium acetate (20 ml) was added and pH was adjusted to 4.3 with 6 M HCl. The mixture was allowed to stand for 30 min and then centrifuged at 20,000 × *g* at 5 °C for 30 min. The supernatant (the liquid whey) was decanted in a separate beaker and kept for further analysis. The precipitate (casein) was washed twice with equal volume of buffer (400 ml water, 20 ml acetic acid (10%, v/v) and 20 ml of 1 M sodium acetate adjusted to pH 4.3) to remove any whey residue in the casein sediment. After every washing step, casein was obtained by centrifugation at 20,000 × *g* for 30 min at 5 °C. The collected supernatant from the washing steps was returned to the liquid whey supernatant collected previously. The washed casein was then freeze dried and stored at −20 °C until used for thermal analysis.

2.5. Preparation of whey protein

Whey protein could be precipitated by ammonium sulfate or ethanol. In this work both techniques were used to determine the difference of thermal characteristics of two types of whey protein. Whey protein obtained by acid precipitation of caseins was divided into two parts; one part was used for salt precipitation (ammonium sulfate, type 1) of whey protein and the other part for alcohol (type 2) precipitation. For salt precipitation, milk sample was saturated with ammonium sulfate, kept inside a fridge (4 °C) over night and then centrifuged (10,000 × *g* at 15 °C for 15 min). The supernatant was discarded and the sediment was collected, freeze-dried and stored at −20 °C. For alcohol precipitation, 95% ethanol was added to milk sample to make final concentration 70% ethanol. The mixture was immediately centrifuged (5000 × *g* for 5 min at 25 °C), supernatant was decanted and whey protein was obtained. Whey protein was freeze dried and supernatant was used for lactose separation.

2.6. Separation of lactose

Lactose was separated similar to the method used by Bund and Pandit [30] with some modification. The lactose was crystallized by keeping the whey-free supernatant (i.e. alcoholic precipitation) in the fridge overnight at 4 °C and then centrifuged at 5000 × *g* for 10 min at 4 °C. Finally lactose crystals were freeze dried and kept at −20 °C until used for analysis.

2.7. Thermal analysis

Freeze drying was performed in a laboratory freeze-drier at 20 °C (i.e. drying from −40 to 20 °C) and 100 Pa. All freeze-dried samples were equilibrated in air-sealed jar maintained at relative humidity 11.3% with a saturated salt solution of lithium chloride in a beaker placed inside the jar. In order to ensure saturated condition in the salt solution, it was always ensured a layer of salt crystals at the bottom of the beaker. The equilibration took for 4 weeks. The samples were stored at −20 °C until used for DSC experiments. Differential scanning calorimetry (DSC) (DSC Q10, TA Instruments, New Castle, DE, USA) were used to measure the glass transition and melting of freeze-dried whole camel milk powder, and other components of camel milk (fat, cream, casein, whey protein and lactose).

The procedures for thermal analysis were similar as discussed by Rahman et al. [31]. Samples of 10 mg placed in a sealed aluminum pan were cooled to −90 °C at 5 °C/min, and kept for 10 min. It was then scanned from −90 to 250 °C (whole and skimmed milk, whey protein precipitate by ammonium sulfate, and lactose) or −90 to 200 °C (casein and whey protein precipitate by ethanol, cream, fat) at a rate of 10 °C/min. In the case of lactose, the initial run did not show any shift in the thermogram line, thus it was difficult to trace the glass transition by this method. Second batch of experiments were conducted as follows: samples of 10 mg placed in a sealed aluminum pan were cooled to −90 °C at 5 °C/min, and kept for 10 min. It was then scanned from −90 to 130 °C at a rate of 10 °C/min (i.e. in order to transform into amorphous state) and annealed for 0.1 to 5 min. After annealing for different predetermined times, the sample was cooled again to −90 °C at 5 °C/min, followed by a heating cycle up to 250 °C at a rate of 10 °C/min. The glass transition (a shift in the thermogram line) and fat-melting or solids-melting (endothermic peak) characteristics were identified from the thermogram. The glass transition was characterized by its initial, mid and end points; and the change of specific heat at the shift. Melting peaks were characterized from initial, maximum slope and peak points and enthalpy involved in the transition. Average and standard deviation of 3–6 replicated were obtained for all experiments, except whole and skimmed milk powders.

3. Results and discussion

3.1. Whole milk powders

Initially thermal characteristics of whole and skimmed camel milk were performed before comparing characteristics of the