



State diagram and water adsorption isotherm of raspberry (*Rubus idaeus*)

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ABSTRACT

Thermal transitions of freeze-dried raspberry powder (*Rubus idaeus*) were analyzed by using differential scanning calorimetry. Freeze-dried raspberry powders containing unfreezable and freezable water were examined to develop the state diagram of raspberry. The state diagram of freeze-dried raspberry powders included the glass line; glass transition temperature versus solids content, freezing curve; initial freezing point versus solids content; end point of freezing T'_m , corresponding solids content X'_s , characteristic glass transition T'_g and corresponding solids contents X''_s of maximally-freeze-concentrated raspberry. The conditions of the maximal-freeze-concentrate obtained from freezing curve corresponded to $T'_m = -38^\circ\text{C}$ and $X'_s = 0.78$ kg solids/kg raspberry and $T'_g = -47^\circ\text{C}$ and $X''_s = 0.82$ kg solids/kg raspberry. The T'_g was determined by extending the freezing curve to glass line. The quantities of unfreezable water identified from enthalpy data and the freezing curve were comparable. Adsorption isotherms of freeze-dried raspberries were determined at room temperature by the isopiestic method and the data was modeled with BET and GAB equations. The BET and GAB monolayer moisture contents were observed to be 0.045 and 0.074 kg water/kg dry raspberry solids, respectively. The state diagram and water sorption properties of raspberries are useful in optimizing the retention of anthocyanins, phenolics concentrations and antioxidant activities in freeze-dried and frozen raspberries during storage.

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1. Introduction

A state diagram of food presents different physical states of food as a function of solids content and temperature. The role of the state diagram of food materials in determining processing and storage stability is highlighted in a number of studies (Rahman 2006; Sablani et al., 2004; Champion et al., 2000; Goff and Sahagian, 1996; Sa and Sereno, 1994; Roos and Karel, 1991; Slade and Levine, 1991). The state diagram consists of a freezing curve of initial freezing point versus solids content, a solubility curve of solids fraction in a saturated aqueous solution at a given temperature, the eutectic point, a glass line of glass transition temperature versus solids content, and conditions of maximal-freeze-concentration (Rahman, 2006). The concept of glass transition was investigated extensively in polymer, material, pharmaceutical and food sciences to relate physical, chemical and structural changes in the physical state of material. Glass transition is a nature of second order time-temperature dependent transition of physical state of a material. During glass transition temperature change, material transforms from a relatively stable glassy state to a metastable rubbery state or vice versa. As a result of the industrial relevance and scientific interest of glass transition research, researchers continue to discuss the application of glass transition as a tool for predicting the

microbiological, physical and chemical changes that occur during processing and storage (Sablani et al., 2007a,b,c; Kasapis et al., 2007; Rahman, 2006; Khalloufi and Ratti, 2003; Champion et al., 2000; Karel et al., 1994; Kerr et al., 1993; Roos and Karel, 1991; Slade and Levine, 1991).

Raspberries (*Rubus idaeus*) are commercial fruits used industrially for formulating jam, jelly, sauce, puree, topping, syrup or juice concentrates. Raspberry fruit is well recognized for health promoting constituents. Raspberries are rich in potential antioxidant phenolic compounds including anthocyanins. Studies evaluated the potential role of raspberries in preventing chronic stress, cancer and heart diseases (Zhang et al., 2005; Wang and Lin, 2000). Anthocyanins and phenolic compounds are susceptible to deterioration during processing and storage conditions (Sadilova et al., 2006). Stability of bioactive compounds during processing and storage is important to the food industry.

Glass transition temperature data are reported for several fruits (tomato, dates, pineapple and grapes) but a complete state diagram using glass lines and freezing curves are reported only for selected fruits (apples, strawberries, grapes and dates) (Bai et al., 2001; Kasapis et al., 2000; Rahman, 2004; Sa and Sereno, 1994; Sa et al., 1999). Khalloufi et al. (2000) examined glass transition temperatures of raspberries, blueberries, strawberries and blackberries as a function of water contents. The glass transition temperatures of the berries decrease as water contents increase. Since soluble solids of berries are mostly sugars, the glass

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transition temperature of the freeze-dried powder is associated with the glass transition temperatures of glucose and fructose. However the studies related to freezing curve and conditions of maximally-freeze-concentration for berries including raspberries are not reported in the literature. This information on maximal freeze concentration of berries is important to develop a complete state diagram useful in studying stability of anthocyanins and other bioactive compounds in frozen and dried raspberries.

The objective of the current study is to develop a state diagram for freeze-dried raspberries by determining glass line (T_g versus total solids content), freezing curve (initial freezing temperature versus total solids content) and maximal-freeze-concentration conditions (T'_m , T'_g and X'_s). In addition, a water adsorption isotherm is determined to evaluate and compare a stability criterion with the concept of glass transition.

2. Materials and methods

Red raspberry fruits (*Rubus idaeus*) grown in Vancouver, WA were collected and frozen immediately at -37°C for 48 h. The frozen raspberries were layered in the metal trays of freeze dryer (Virtis freeze mobile 24 with Unitop 600 L, VirTis SP Industries Co., New York) to decrease the water content. The shelf temperature was set at -20°C with a vacuum of 20 Pa. The temperature of the condenser was adjusted to -60°C . After 48 h of freeze drying, the raspberries were removed and ground immediately to a fine powder with a mortar and pestle. The moisture content of the raspberry powder was 0.042 kg H_2O /kg raspberry. The raspberry powder was placed in open weighing bottles and equilibrated for three to four weeks with saturated salt solutions of constant water activities in airtight containers (volume: $2.5 \times 10^{-3} \text{ m}^3$) at room temperature (23°C). The salts used were: LiCl, CH_3COOK , MgCl_2 , K_2CO_3 , MgNO_3 , NaNO_2 , NaCl and KCl (Fisher Scientific, Houston, TX) with equilibrium relative humidities of 11.3%, 22.5%, 32.8%, 43.2%, 52.9%, 65.8%, 75% and 86%, respectively. Relative humidity values for the saturated salt solutions were obtained from Greenspan (1977). A small amount of thymol was placed inside the airtight containers to avoid microbial growth in raspberry powders.

After equilibration triplicate of 1 g raspberry powder samples were used to determine the water content in a vacuum oven. For this, raspberry powders in aluminum weighing dishes were placed inside a vacuum oven at 80°C for 10 h. The pressure inside the chamber was 10 kPa. The dried raspberry powders obtained after vacuum oven drying were stored under dark and dry conditions for thermal transition experiments. Triplicate samples of high moisture raspberry powders (0.30, 0.40, 0.50, 0.60, 0.70 and 0.80 kg H_2O /kg raspberry) were prepared by adding precalculated amount of distilled water to the dried raspberry powders obtained after the freeze drying. The raspberry powders were mixed with water in a small beaker and sealed with aluminum foil to avoid moisture loss. The prepared raspberries were equilibrated at 4°C for 24 h before experimentation.

2.1. Determination of thermal transitions

The thermal transition experiments in freeze-dried raspberry powder were conducted with a differential scanning calorimeter (DSC, Q2000, TA Instruments, New Castle, DE). The calorimeter was calibrated by checking standard temperatures and enthalpies of fusion for indium and sapphire. The raspberry powders were cooled by a mechanical refrigerated cooling system. An empty sealed aluminum pan was used as a reference in each test. Following equilibration, 10–20 mg raspberry powders were sealed in aluminum pans (volume 30 μL) and cooled from room temperature to

-90°C at $5^\circ\text{C}/\text{min}$ and equilibrated for 10 min. Raspberry powders were scanned from -90°C to 70°C at a rate of $5^\circ\text{C}/\text{min}$. Initially selected sample with moisture content of 0.034 kg H_2O /kg raspberry powder was scanned at 1, 2, 5, 10 and $20^\circ\text{C}/\text{min}$ and scan rate of $5^\circ\text{C}/\text{min}$ was selected for subsequent analysis. The scan rate of $5^\circ\text{C}/\text{min}$ is commonly used for determination of glass transition temperature. DSC produces heat flow (W/g) versus temperature thermograms. The glass transition temperature (T_g) is identified as a (vertical) shift in the heat flow curve of thermogram. TA Instruments Universal analysis software was used to analyze the onset, mid and end-points of the glass transition. Three replicates were used for the determination of glass transition temperatures at each water content/water activity. In addition, freeze-dried raspberry powders with moisture of 0.042 kg H_2O /kg raspberry were further dried in a vacuum oven to obtained raspberry powder with no moisture for thermal analysis. For high moisture raspberry powders, thermograms provide melting endotherms along with glass transition temperatures. The area of the melting endotherm peaks provides the enthalpy of melting (ΔH_m) determined by drawing a linear base line to the endotherm. The intersection point of the baseline with the left side of the endotherm was taken as the end point of freezing (T'_m) of the raspberries. High moisture raspberry powders (0.3–0.8 kg H_2O /kg raspberry) were subjected to annealing at a temperature ($T'_m - 1$) for 30 min during a DSC scan. Initially annealing was performed on raspberries with moisture content of 0.4 kg H_2O /kg raspberry at a temperature ($T'_m - 1$) for 0, 30 and 60 min and an annealing time of 30 min was chosen for further analysis. After annealing, freeze-dried raspberry powders were scanned from ($T'_m - 1$) to -90°C at the rate of $5^\circ\text{C}/\text{min}$. From -90°C to 70°C , raspberries were scanned at a rate of $5^\circ\text{C}/\text{min}$. A tangent to the left side of the endotherm curve was drawn to identify the freezing point (T_f) of the high moisture raspberries (Rahman, 2004; Bai et al., 2001).

2.2. Water sorption and thermal transitions modeling

Several theoretical (BET, GAB model etc.) and empirical equations (Oswin, Henderson model etc.) are available for modelling of sorption isotherms data. In the present study water adsorption data of freeze-dried raspberry powder was modeled using most commonly used Brunauer–Emmett–Teller (BET) and Guggenheim–Andersen–de Boer (GAB) equations (Rahman, 1995). Both of these models have sound theoretical background and their parameters provide physical meaning related to the sorption process compared to the empirical models (Labuza and Altunakar, 2007). These two models are based on the monolayer moisture concept and provide the value of the monolayer moisture content of the material, considered the safe moisture for dried foods during preservation, but most other models lack this parameter. The BET equation is

$$M_w = \frac{M_b B a_w}{(1 - a_w)[1 + (B - 1)a_w]} \quad (1)$$

where M_w is the water content (kg water/kg dry solids); M_b is the BET monolayer water content (kg water/kg dry solids); and B is a constant related to the net heat of sorption. The value of B is normally less than 2 for type III isotherms and varies between 2 and 50 for type II isotherm. The BET isotherm is applicable between water activities of 0.05 and 0.45, an adequate range for the calculation of parameters M_b and B (Rahman, 1995). The GAB equation is

$$M_w = \frac{M_g C K a_w}{[(1 - K a_w)(1 - K a_w + C K a_w)]} \quad (2)$$

where M_g is the GAB monolayer water content (dry basis). C is a constant related to the monolayer heat of sorption and the value

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