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Water sorption and glass transition temperatures in red raspberry (*Rubus idaeus*)

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ABSTRACT

Water sorption isotherms and glass transition temperatures of raspberries were determined to understand interactions between water and biopolymers. Water adsorption and desorption isotherms of raspberries were determined with an isopiestic method. Thermal transitions of raspberries equilibrated at selected water concentrations using adsorption and desorption were determined by differential scanning calorimetry (DSC). The sorption isotherm data were modeled by BET and GAB equations, while the plasticizing influence of water on glass transition was modeled by the Gordon–Taylor equation. Equilibrium water concentrations varied at equivalent water activities during adsorption and desorption indicating occurrence of hysteresis and irreversibility of thermodynamic processes. The monolayer water concentrations of 0.099 and 0.108 kg water/kg dry raspberry solids obtained by BET and GAB models during desorption were larger than those during adsorption (0.059 and 0.074 kg water/kg dry raspberry solids). The glass transition temperature of raspberries decreased with increasing water concentrations. The Gordon–Taylor parameters T_{gs} and k obtained for raspberries during adsorption were 42.6 °C and 4.73 and during desorption were 44.9 °C and 5.03, respectively. The characteristic glass transition temperature of the maximally freeze concentrated solution T_g' was -63.1 ± 5 °C and the onset of ice crystal melting temperature T_m' was -32.3 ± 0.4 °C. Although the water activity differed significantly at equivalent water concentrations obtained using absorption or desorption, the glass transition temperatures of raspberries were dependent on the concentration of water present not the method of equilibration.

1. Introduction

Water plays a central role as a solvent for biochemical reactions in foods under a wide range of conditions attributed to remarkable characteristics of water such as excellent solvency, plasticity and large specific heat, enthalpy of phase change, dielectric constant, and surface tension. A better understanding of the interactions among water and food macromolecules is of fundamental importance to the stability of high solids food systems. Water–solids equilibria, particularly sorption behavior of water in foods, observed using a thermodynamic approach is commonly related to physical, chemical and microbiological stability of dehydrated foods [1,2]. According to the equilibrium concept, bound water, defined as solute associated water that differs thermodynamically from pure/bulk water, exhibits reduced solubility for other compounds causing a reduction of the diffusion of water soluble solutes in sorbents [3]. Therefore, foods may be biochemically more stable when they contain only bound water with no free water. Bound water is characterized by low vapor pressure, large binding energy as determined during dehydration, reduced mobility as observed by nuclear magnetic resonance (NMR), unfreezability at low temperatures, and unavailability as a solvent [4].

The water sorption behavior of foods is not fully reversible as indicated by sorption hysteresis. Hysteresis in sorption indicates that at a given water activity and temperature an adsorbent holds a smaller amount of water during an adsorption process than during a desorption process. The extent of hysteresis is related to the nature and state of components in a food. Hysteresis may reflect the structural and conformational rearrangement of components, which alters the accessibility of energetically favorable polar sites, and thus may hinder the movement of water [1]. Hysteresis may implicate the physicochemical stability of foods. Lipid oxidation of foods at constant water activity occurred 3–6 times faster in foods prepared by desorption than in foods prepared by adsorption [5].

It is argued that low-water content foods exist in a state of pseudo-equilibrium as evidenced by the existence of hysteresis, and kinetic factors may be observed to evaluate long-term storage stability of dehydrated foods expressed as glass transition temperatures (T_g) [6–9]. At glass transition temperatures, it is considered that foods transform from a relatively stable glassy state to a rubbery state or *vice versa*. In the glassy state, below T_g, the mobility of

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Table 1
Glass transition temperatures of raspberry samples at selected water activities and water contents after adsorption and desorption experiments.

Adsorption				Desorption			
Water activity, a_w (fraction)	Water content (kg water/kg raspberry)	T_{gi} (°C)	T_{gm} (°C)	Water activity, a_w (fraction)	Water content (kg water/kg raspberry)	T_{gi} (°C)	T_{gm} (°C)
0.113	0.034 ± 0.000^a	17.5 ± 1	19.2 ± 1	0.113	0.054 ± 0.003^c	11.5 ± 2	15.4 ± 1
0.225	0.046 ± 0.001^b	7.3 ± 1	9.5 ± 1	0.225	0.066 ± 0.001^d	3.4 ± 2	6.6 ± 2
0.328	0.069 ± 0.001^e	−5.03 ± 1	−4.2 ± 2	0.328	0.080 ± 0.001^f	−11.4 ± 2	−8.4 ± 3
0.432	0.086 ± 0.001^g	−12.0 ± 5	−11.2 ± 6	0.432	0.089 ± 0.001^h	−16.6 ± 4	−13.7 ± 6
0.529	0.112 ± 0.001^i	−19.4 ± 6	−16.3 ± 6	0.529	0.126 ± 0.004^j	−34.0 ± 4	−33.3 ± 6
0.658	0.134 ± 0.003^k	−29.7 ± 6	−28.7 ± 7	0.658	0.138 ± 0.001^l	−52.1 ± 2	−48.1 ± 1
0.750	0.175 ± 0.001^m	−57.0 ± 0	−53.9 ± 2	0.750	0.367 ± 0.011^o	–	–
0.860	0.242 ± 0.007^n	−65.5 ± 4	−62.1 ± 4	0.860	0.484 ± 0.007^p	–	–

Different superscripts represent statistical significant differences between water contents of raspberries obtained at selected water activities by adsorption and desorption ($p < 0.05$).

water and the rate of deteriorative reactions are reduced drastically and foods are stable for extended time periods. The role of T_g as a physicochemical parameter for control of microbiological, physical and biochemical changes is subjected to several investigations [10–16].

Raspberries represent a large group of high sugar small fruits for which storage stability at low-water content is important. The objective of this research was to analyze water sorption and glass transition temperatures during adsorption and desorption of red raspberries.

2. Materials and methods

2.1. Preparation of raspberries

Washington grown red raspberry fruits were obtained from the local market and frozen at −37 °C for 2 days. The frozen raspberries were dried using a laboratory freeze dryer (Virtis freeze mobile 24 with Unitop 600L, VirTis SP Industries Co., New York, NY) to a water content of 0.042 kg H_2O/kg raspberry solids. The condenser temperature was adjusted to −60 °C and the shelf temperature was set at −20 °C with a pressure of 20 Pa. After 2 days, raspberries were removed from the freeze drier and ground to a fine powder using a mortar and pestle. The raspberry powder was placed in open weighing bottles and equilibrated for 3–4 weeks with saturated salt solutions of constant water activities in airtight containers at room temperature (23 °C) for adsorption studies. The salts used were: LiCl, CH_3COOK, $MgCl_2$, K_2CO_3, $MgNO_3$, $NaNO_2$, NaCl and KCl (Fisher Scientific, Houston, TX). The equilibrium relative humidity in the containers varied from 11.3 to 86% for adsorption and desorption experiments [17]. The corresponding water activity values are presented in Table 1. A small amount of thymol in a small bottle was kept inside the airtight containers to prohibit microbial growth in raspberry powders.

For desorption studies, fresh raspberries (0.85 kg water/kg raspberry) with known weight were dried to a water content approximately of 0.40 kg water/kg raspberry in laboratory vacuum oven at 70 °C (Yamato ADP-31, Yamato Scientific America Inc., CA, USA). Weights of the raspberry samples were determined at selected time intervals of drying to ensure the final water content (0.40 kg water/kg raspberry). After drying, raspberries were immediately placed inside airtight containers with saturated solutions for equilibration. The raspberry samples were exposed to super saturated solutions to achieve constant water activity values at room temperature (23 °C). Saturated solutions used were the same as for the adsorption experiments. Initially mold growth was observed for raspberry samples stored at 0.75 and 0.86 water activities. These contaminated samples were discarded and raspberry samples were prepared again for the experiments. For this, the raspberries were washed in 300 ppm of chlorine water and the experiments were conducted inside a biological safety cabinet under sterilized environment.

After 3–4 weeks of equilibration at selected relative humidity values, water content of the raspberry samples obtained by adsorption and desorption experiments were determined by vacuum oven method. For this, triplicate raspberry samples in aluminum weighing dishes were heated inside a vacuum oven at 80 °C for 10 h with 10 kPa chamber pressure.

2.2. Thermal analysis

A differential scanning calorimeter (DSC, Q2000, TA Instruments, New Castle, DE) was used to analyze the thermal transitions in raspberry samples obtained after adsorption and desorption experiments. The calorimeter was calibrated by checking standard temperatures and enthalpies of fusion for indium and sapphire. An empty sealed aluminum pan was used as a reference in each test. Nitrogen gas at a flow rate of 50 ml/min was used as the purge gas to avoid water condensation around the raspberry sample. Ten to fifteen milligrams of raspberry sample was sealed in aluminum pans (capacity 30 μL) and cooled from room temperature to −90 °C at 5 °C/min for formation of glassy state in raspberry sample and equilibrated for 10 min. 5 °C/min is the commonly followed cooling and heating rate of the thermal analysis of food systems. The raspberry samples were scanned from −90 °C to 70 °C at a rate of 5 °C/min and cooled back to 25 °C at a rate of 5 °C/min. DSC thermograms, presenting the heat flow (W/g) and temperature relationship were used to analyze the thermal transitions in raspberries during heating and cooling. The glass transition temperature (T_g) is identified as a (vertical) shift in the heat flow-temperature relationship. TA Instruments Universal analysis software was used to analyze the onset, mid and end points of the glass transition. Triplicate samples of raspberry after adsorption and desorption experiments were used to determine the glass transition temperatures at each water content/water activity.

For high water content raspberry samples ($\geq 0.75\, a_w$) obtained in desorption experiments, the onset of melting of ice crystals (T'_m) was determined by DSC scanning of raspberry samples. The raspberry samples were cooled without annealing to identify the apparent T'_m as presented in Fig. 1 [18]. A linear base line to the melting endotherm is drawn to identify apparent T'_m. The baseline intersects with the endotherm and the intersection at the left side was taken as the apparent T'_m of the raspberries as presented in Fig. 1 [18,32]. For high water content samples, characteristic glass transition temperature (T'_g) is associated with the maximal freeze concentrate (Fig. 1). Annealing was performed for high water raspberry samples after desorption experiments at a temperature (apparent $T'_m - 1$) for 30 min during DSC scan to obtain

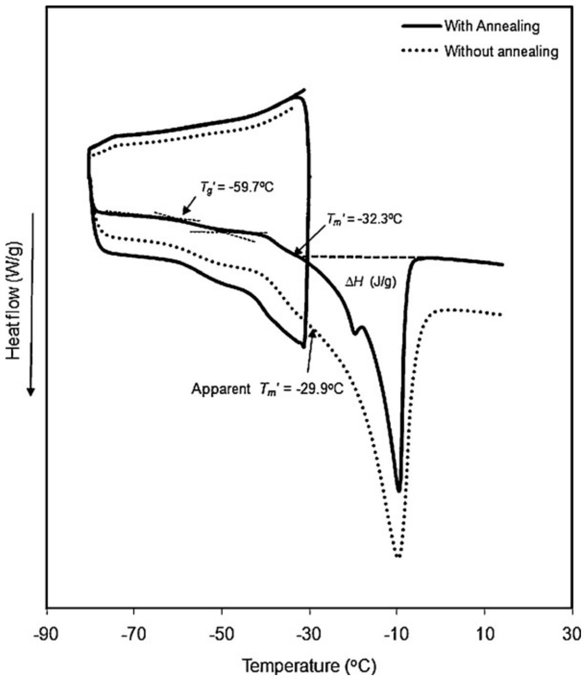

Fig. 1. Melting endotherm, T'_m and T'_g associated with raspberry sample equilibrated by desorption at water activity of 0.75 (with and without annealing).

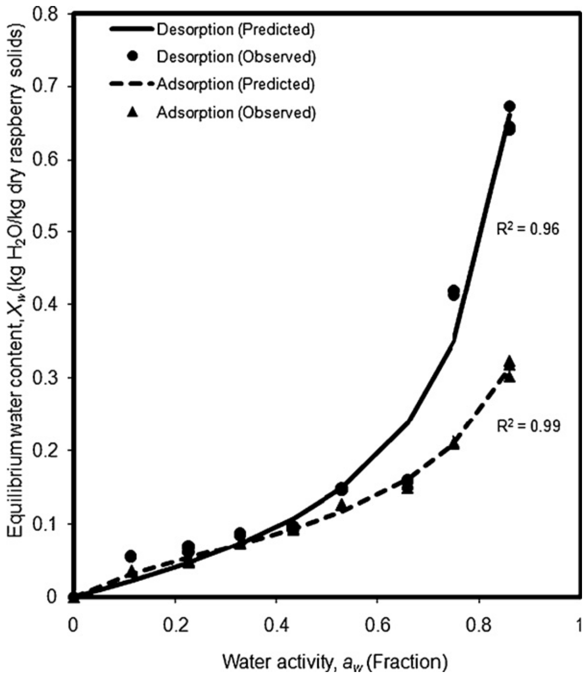

Fig. 2. Water adsorption and desorption isotherms of raspberries at 23 °C.

maximum ice formation (Fig. 1). Raspberry samples were scanned from (apparent $T'_m - 1$) to −90 °C at the rate of 5 °C/min. Raspberry samples after desorption were scanned from −90 °C to 70 °C at a rate of 5 °C/min [18,19]. The T'_m and T'_g were determined from the same experiment where the sample was annealed for 30 min (Fig. 1).

2.3. Modeling

Brunauer–Emmett–Teller (BET) and Guggenheim-Anderson-de Boer (GAB) models are widely accepted to fit water sorption data of food materials. BET and GAB models are based on the monolayer water concept and derive the monolayer water content from water activity-water content by non-linear optimization. To model the water adsorption and desorption data of dried raspberry samples, BET and GAB models were used [20]. The BET equation is

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

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 of water. The BET isotherm is accurate for foods with water activities between 0.05 and 0.45, though a small but adequate range for the calculation of parameters M_b and B. The GAB isotherm equation is an extension of the BET model and can be used for foods with water activities from 0 to 0.9 by taking into consideration of multilayer adsorption. The GAB equation is considered one of the best fitting equations to model the sorption isotherms of many foods

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

where M_g is the GAB monolayer water content (dry basis). For type III isotherms, generally the value of the constant C lies between 0 and 2 while for type II isotherms, the $C > 2$. K is a factor related to the multilayer heat of sorption generally between 0 and 1. Non-linear optimization by Windows Excel® was used to obtain the three parameters in GAB using two variables (i.e. water content and water activity).

In low-water food systems such as dry raspberries, T_g of the food system decreases sharply with water content. Water plasticization effects in foods may be approximated generally by the Gordon and Taylor equation [21]. For binary food mixtures, considering food total solids and water, The Gordon–Taylor equation is expressed as

$$T_{gm} = \frac{X_s T_{gs} + k X_w T_{gw}}{X_s + k X_w} \tag{3}$$

For aqueous binary mixtures, T_{gm}, T_{gs} and T_{gw} are the glass transition temperatures of the mixture, solids and water, respectively; X_w and X_s are the wet basis water and total solids contents, and k the Gordon–Taylor parameter. Large values for k in a binary mixture indicate large plasticizing effect of the solids by water. The model parameters (k and T_{gs}) of Eq. (3) are estimated using non-linear optimization while considering $T_{gw} = -135$ °C.

Statistical analysis was conducted using SAS®9.1 (SAS Institute, Inc., Cary, NC) computer programme. Analysis of variance (ANOVA) was employed for the samples with a value of $p < 0.05$ being considered statistically significant. The Fisher's LSD (least significant difference) method was used together for this purpose [22]. In addition, statistical *F*-Test was conducted to confirm the statistical significance.

3. Results and discussion

3.1. Water adsorption and desorption isotherms

Water adsorption and desorption isotherms of raspberry exhibited sigmoid shape behavior (Fig. 2). A considerable difference in water contents of raspberry was observed during adsorption and desorption processes indicating hysteresis ($p < 0.05$). The difference in the water contents during adsorption and desorption was more prominent at low ($a_w = 0.11$–0.33) and high ($a_w = 0.75$–0.86) water activities. At the intermediate level of water activities, the difference in water contents between adsorption and desorption processes was smaller. A number of hysteresis loop shapes are observed in food systems depending on the composition and mea-

Table 2
GAB and BET equations parameters for adsorption and desorption data of selected fruits.

Product	Treatment	GAB model			Treatment	BET model	
		M_o kg water/kg raspberry solids	C	K		M_o kg water/kg raspberry solids	B
Raspberry[a]	Adsorption at 23 °C	0.074	5.53	0.904	Adsorption at 23 °C	0.059	9.08
	Desorption at 23 °C	0.108	1.78	0.990	Desorption at 23 °C	0.099	2.23
Strawberry[b]	Adsorption at 30 °C	0.051	3.5	1.16	Adsorption at 30 °C	–	–
	Desorption at 30 °C	0.098	4.9	0.99	Desorption at 30 °C	0.095	5.2
Kiwi fruit[c]	Adsorption at 30 °C	0.047	8.7	1.20	Adsorption at 30 °C	0.058	7.0
	Desorption at 30 °C	0.042	13.3	1.23	Desorption at 30 °C	0.053	8.9
Blanched apple[d]	Adsorption at 25 °C	0.076	1.18	1.03	Adsorption at 25 °C	–	–
	Desorption at 25 °C	0.138	1.54	0.97	Desorption at 25 °C	–	–
Blanched papaya[d]	Adsorption at 25 °C	0.131	1.82	0.98	Adsorption at 25 °C	–	–
	Desorption at 25 °C	0.134	1.57	0.98	Desorption at 25 °C	–	–
Banana[e]	Adsorption at 30 °C	–	–	–	Adsorption at 30 °C	–	–
	Desorption at 30 °C	0.074	18	0.92	Desorption at 30 °C	–	–

[a] Current Study; BET models, $R^2 = 0.96$ for adsorption and desorption data; GAB models, $R^2 = 0.99$ for adsorption data and $R^2 = 0.96$ for desorption data.
[b] Moraga et al. [32].
[c] Moraga et al. [27].
[d] Lopez-Malo et al. [50].
[e] Katekawa and Silva [51].

surement temperature of water sorption. A wide difference in the magnitude and extent of hysteresis of dehydrated foods is reported [23]. In high sugar foods, the hysteresis phenomenon is more pronounced in the low-water activity range ($a_w < 0.6$) [24].

The water adsorption and desorption behavior of selected fruits were modeled using BET and GAB equations (Table 2). Sorption data of raspberry during adsorption and desorption were fitted to BET ($R^2 = 0.96$ for adsorption and desorption data) and GAB models ($R^2 = 0.99$ for adsorption data and $R^2 = 0.96$ for desorption data). Only experimental data with $a_w \leq 0.45$ were fitted well to the BET equation [25]. The BET monolayer water content during adsorption and desorption were 0.059 and 0.099 kg water/kg raspberry solids, respectively, while GAB monolayer values for adsorption and desorption were 0.074 and 0.108 kg water/kg raspberry solids, respectively (Table 2). The constants of BET and GAB equations obtained for raspberry samples during adsorption and desorption were similar to the other selected dry fruits (Table 2). The monolayer water content obtained by GAB is generally larger than the BET monolayer water content [26]. However, an opposite trend was observed with kiwi fruit where the monolayer water content obtained using the GAB equation was smaller than the monolayer water content of kiwi fruits determined with the BET equation [27]. Even though the GAB model is an extension of the BET model, the monolayer water content obtained from BET equation is generally considered as the optimal water content for stability of foods containing large concentrations of solids [28,29]. The monolayer water contents obtained by the BET as well as the GAB model during desorption were larger than the monolayer water contents obtained during adsorption. The difference in water content could be attributed to the presence of greater water content present in the food matrices during desorption compared to adsorption with an equivalent water activity, however according to the water activity concept, the availability of water participating in selected reactions is expected to be equivalent.

3.2. Glass transition temperatures

Thermogram data obtained from the DSC were used to identify glass transition temperatures of raspberry samples equilibrated at selected water activities/water contents (Table 1). Experimental thermograms exhibited glass transitions associated with the amorphous soluble compounds (glucose and fructose) in raspberry samples. DSC thermograms (Fig. 3) for freeze-dried raspberry samples were similar to the DSC curves reported in the literature for other fruits in equivalent ranges of water activities [27,30–33]. For high water content raspberry samples ($\geq 0.75a_w$) in desorption experiments, thermograms provide melting endotherms along with glass transition temperatures, indicating the presence of freezable water in the sample. For high water content raspberries, annealing was performed at a temperature (apparent $T'_m - 1$) for 30 min during the DSC scan for maximum ice formation [34]. The onset of ice crystal melting of raspberry sample with equivalent water activity of 0.75 by desorption is presented in Figs. 1 and 3. The mean value of the onset of ice melting evaluated from desorption samples with a_w 0.75 and 0.86 was considered as T'_m of raspberry was -32.3 ± 0.4 °C. For raspberry samples of $a_w \geq 0.75$

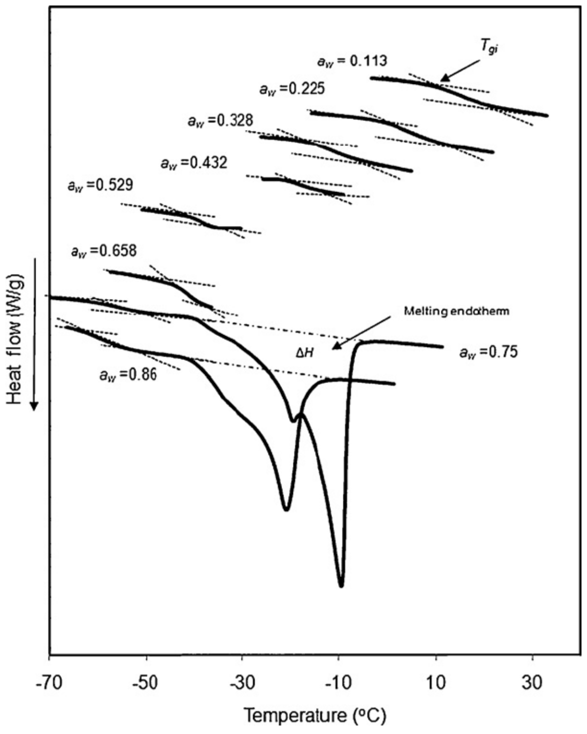

Fig. 3. DSC thermogram presenting heat flow versus temperature of raspberry samples equilibrated by desorption at different water activities.

Table 3
Parameters of Gordon and Taylor equation fitted to glass transition temperatures and water content data of selected fruits during adsorption and desorption.

Product	Treatment	Gordon and Taylor equation parameters	
		T_{gs} (°C)	k
Raspberry[a]	Adsorption	42.6	4.73
	Desorption	44.9	5.03
Strawberry[b]	Adsorption	28.1	4.14
	Desorption	63.0	4.82
Kiwi fruit[c]	Adsorption	40.6	4.84
	Desorption	39.1	4.90
Plum (skin + pulp)[d]	Adsorption	102.7	3.76
	Desorption	–	–
Gooseberry[e]	Adsorption	23.2	5.72
	Desorption	–	–
Apple[f]	Adsorption	41.3	3.59
	Desorption	–	–
Pineapple[g]	Adsorption	57.8	0.21
	Desorption	–	–

[a] Current study.
[b] Moraga et al. [32].
[c] Moraga et al. [27].
[d] Telis et al. [52].
[e] Wang et al. [53].
[f] Bai et al. [19].
[g] Telis and Sobral [54].

by desorption, the glass transition temperature is identified as characteristic glass transition temperature T_g' of maximally freeze concentrated raspberry (Fig. 1). The mean value of the T_g' evaluated in samples with a_w 0.75 and 0.86 considered as the T_g' of raspberry was −63.1 ± 5 °C. Both T_g' and T_m' values were obtained from the same experiments. T_g' and T_m' are not dependent on the water content of the sample. However, some difference was observed in T_g' and T_m' values obtained for samples equilibrated at a_w of 0.75 and 0.86 attributed to experimental variability. Some researchers have also noted a little difference in T_g' and T_m' values at different water contents [18,19,35]. For instance, Bai et al. [19] observed T_g' of apple samples as −61.6 and −58.4 °C for water contents of 0.856 and 0.732 kg water/kg sample, respectively. Also Syamaladevi et al. [33] observed T_g' of raspberry as −57.4 and −55.8 °C for water contents of 0.7 and 0.6 kg water/kg raspberry, respectively. No endotherms associated with sugar crystallization or melting were observed. Crystallization of amorphous sugars results in the loss of adsorbed water if anhydrous crystals are formed [36,37]. The water sorption isotherms did not exhibit discontinuities resulting from crystallization, thus indicating the kinetic stability of the amorphous sugars in raspberry [32]. The onset of glass transition temperature (T_{gi}) decreased from 17.5 °C to −65.5 °C as water content of the freeze-dried raspberry solids increased from 0.034 to 0.242 kg water/kg raspberry during adsorption. Fresh raspberries contain 84.5% water, 13.4% carbohydrate, 1.30% protein, 0.3% fat and 0.5% ash [38]. Glucose and fructose are the major sugars present in raspberries. So the glass transition temperatures in raspberries may be related to the T_g of glucose and fructose. The glass transition temperatures and thermograms of freeze-dried raspberries are similar to the glass transition temperatures and thermograms of glucose and fructose [37,39,40]. The effect of water content on glass transition is fitted by the Gordon–Taylor equation [21]. The Gordon–Taylor constants T_{gs} and k (Eq. (3)) obtained for raspberry samples during adsorption were 42.6 °C and 4.73, while the T_{gs} and k during desorption were 44.9 °C and 5.03, respectively (Table 3). The depression in glass transition temperatures with increasing water content is due to the plasticization effect of water on the amorphous constituents of the raspberry matrices (Fig. 4; $R^2 = 0.93$ for adsorption data and $R^2 = 0.89$ for desorption data). T_g' values were not included while fitting the Gordon–Taylor equation for glass transition temperature and solids content data obtained the sample equilibrated with desorption process. The glass transition temperature of anhydrous raspberry solids (T_{gs}) is greater than the T_{gs} of glucose and fructose which can be attributed to the effect of other amorphous soluble biopolymers with higher T_{gs}, the interactions among the compounds and the complex structure of raspberry solids.

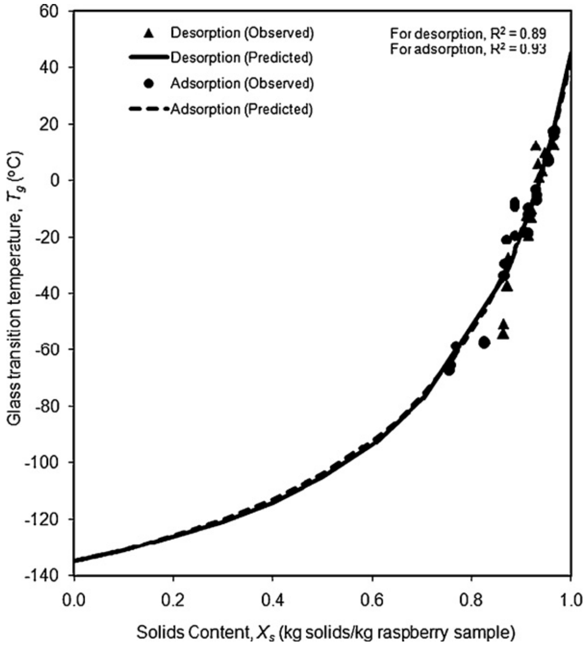

Fig. 4. Effect of solids content on glass transition temperatures of raspberries equilibrated by adsorption and desorption.

3.3. Water activity, glass transition temperature and water content relationships

Water activity is measured when the food system is in thermodynamic equilibrium with the surroundings. One of the main factors influencing the stability of foods during processing and storage is the amount of water in multicomponent food systems. Studies are conducted to probe the influence of quality of water characterized as water activity and quantity of water characterized as water content [5,41–44]. The water activity determined using the thermodynamic approach is related to the microbiological and biochemical activity in foods. For example, microorganisms do not grow at water activity less than 0.6. A food product may be most stable at its monolayer water content, which may vary with chemical composition and physical structure [45]. Experimental studies demonstrate equivalent water activities exhibit different equilibrium water contents during adsorption and desorption in foods, indicating hysteresis or irreversibility of the sorption process. In the present study, hysteresis was observed as expected in water sorption of raspberry samples (Fig. 2). During desorption, at equivalent water contents smaller vapor pressure is observed than the vapor pressure observed during the adsorption process. Hysteresis in foods may be due to the changes in internal structural configuration and conformational rearrangements at the molecular level or by the irreversible changes in structure during the making of foods by adsorption or desorption. Several factors including components, temperature and pretreatments control hysteresis. Several theories address the hysteresis phenomena in foods such as incomplete wetting, ink bottle and open pore theories [46]. It is difficult to provide a single reason for the hysteresis phenomena in foods due to the fact that food is a complex mixture of various components, which not only absorb water independently but also interact [47]. The thermodynamic approach suggests water activity is more relevant than total quantity of water in defining the perishability and stability of foods. In foods containing equivalent water contents, the reactive water solvent for physical, microbiological or biochemical reactions is dependent on whether the food is equilibrated using adsorption or desorption.

Glass transition concept is related to the kinetic theory which observes the molecular relaxation and rearrangement during glass to rubber transitions in a food system. Glass transition temperature is a characteristic of nonequilibrium amorphous food systems. Water drastically reduces the glass transition temperature of a food system. The decrease in glass transition temperature in raspberry by water addition might be due to the increased free volume between the molecules. The decrease in glass transition temperature of raspberry samples indicates that the T_g of raspberry samples was primarily influenced by the concentration of water, not by the equilibration process (Table 1 and Fig. 4). The glass transition temperatures of raspberry samples with equivalent water activities were greater after adsorption than desorption due to smaller water concentrations (Fig. 5). Water is a strong plasticizer and has a low molecular weight and glass transition temperature (−135 °C) compared to the raspberry solids. The water content in raspberry samples equilibrated during desorption was higher than the sample equilibrated with adsorption process. Statistical analysis indicated that the glass transition temperature of raspberries is influenced by water content only and not by the equilibration method ($p > 0.05$). On the other hand, adsorption and desorption isotherms of raspberries present the water activity is influenced by the equilibration process, presented by the hysteresis.

Moraga et al. [27] observed similar behavior for water sorption and plasticization of kiwi fruit. However, in an earlier study Moraga et al. [32] noted the opposite behavior, i.e. the glass transition temperatures of strawberries were influenced more by water activity than by water content [32]. The discrepancy in plasticization behavior of water in selected fruits was attributed to differences in soluble and insoluble solid components in fruits. In the case of strawberries, the concentration of water in strawberries during adsorption and desorption was significantly different. However, the net plasticization effect of water on soluble components was negligible. Some of the water may be present in other phases (insoluble structural polymers) and contributing little to plasticization of the amorphous soluble solids [32].

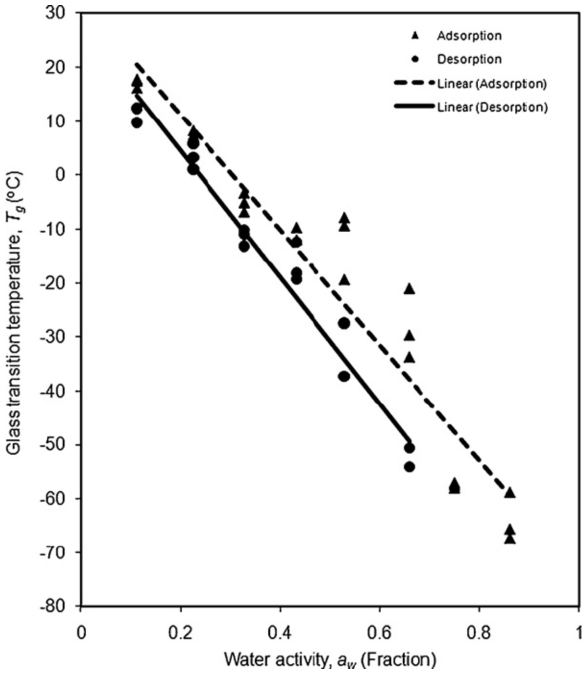

Fig. 5. Influence of water activity on onset of glass transition temperature of raspberries during adsorption and desorption.

It is important to consider that water activity is a property of water molecules while glass transition is associated with amorphous food systems. To elucidate the water activity–water content–glass transition relationships of complex multicomponent food systems such as fruits and vegetables, the definition of an idealized model of the fruits may be useful [32]. The two main phases in the idealized model of the fruit are aqueous liquid phase containing soluble solids and water insoluble phase. At equilibrium, different phases in the system will have the same water activity but the amount of water present in each phase can be different depending on the level of structural changes which occur in each phase of raspberries during freeze drying. The water content at equilibrium is the average value of the aqueous phase and water insoluble phase while water activity is global and same for these two phases. The water retained by insoluble phase contributes to the mean water content but does not contribute in plasticizing, i.e. lowering the T_g of the amorphous soluble solids. During freeze drying, rupture of cell walls and membranes can cause differences in water binding capacity of each phase resulting in hysteresis during adsorption and desorption processes. The total amount of insoluble solids in raspberry fruits is very small, which is only 5% of the total solids compared to 95% of soluble solids [38]. So the T_g of raspberry is associated with the mean T_g of aqueous phase consisting the soluble solids associated with raspberry [32]. So variation in T_g is associated with the aqueous phase of a fruit system while, the water activity is same for different phases at equilibrium (aqueous phase and water insoluble phase).

A small increase in water content of a food may produce a large depression of glass transition temperature due to the water plasticization effect. Intermediate moisture foods prepared by adsorption may be in glassy state, while a food with an equivalent water activity prepared by desorption may be in the rubbery state as a result of greater water content. The decrease in the viscosity of the rubbery state compared to the glassy state may improve the molecular mobility and reaction rates of the foods prepared by desorption rather than adsorption at equivalent water activity.

Caking of inulin powder was observed at a critical water activity of 0.56 and greater during adsorption, while caking was observed for desorption for all the water activities [43]. Before the desorption isotherm experiments, the inulin powders were stored at a high relative humidity (94%), then transferred to chambers with 0, 12, 33, 59, 75 or 94% RH for desorption experiments. During the initial conditioning at 94%, all the inulin powder was caked leading to solid bridges and an irreversible solid during the desorption experiments [48]. Van Nieuwenhuijzen et al. [44] reported that both water activity and water content or the history of bread may control the crispness of bread crust. The mobility of water in bread crust determined by NMR analysis does not change at constant water contents and selected water activities obtained by adsorption and desorption experiments. They reported that glass transition temperature of bread crust is dependent on water content and independent of water activity. However, molecular mobility and loss of crispness occurs in the glassy state of foods [49]. Limited studies are available simultaneously evaluating both water activity and glass transition aspects of food stability. More experimental and theoretical studies such as nuclear magnetic resonance and electron paramagnetic resonance spectroscopy are necessary to probe the water dynamics in foods.

4. Conclusions

Equilibrium water contents were larger during desorption compared to adsorption of freeze-dried raspberry samples at equivalent water activity indicating hysteresis and thermodynamic irreversibility. The monolayer water content during desorption were larger than the monolayer water content during adsorption. The glass transition temperature of raspberry samples decreased with increasing water contents due to the plasticization effects of water. The raspberry samples equilibrated at water activities of 0.75 and 0.86 during desorption contained freezable water. The fresh raspberries may be kept below $-63\,^{\circ}\mathrm{C}$ (T'_g) to avoid ice recrystallization and maintain their quality after thawing. At equivalent water contents obtained by absorption or desorption processes, the glass transition temperature of raspberry sample was dependent on the concentration of water in raspberry sample and not the method of water equilibration. The present study indicated substantial differences between water activity and glass transition approaches to characterization of molecular interactions between water and biopolymers in raspberry. Additional research is needed to provide insight into the manifestation of water mobility in food matrices.

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