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Sorption isotherms, thermodynamic properties and glass transition temperature of mucilage extracted from chia seeds (*Salvia hispanica* L.)

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ABSTRACT

Freeze-dried chia mucilage adsorption isotherms were determined at 25, 35 and 40 °C and fitted with the Guggenheim–Anderson–de Boer model. The integral thermodynamic properties (enthalpy and entropy) were estimated with the Clausius–Clapeyron equation. Pore radius of the mucilage, calculated with the Kelvin equation, varied from 0.87 to 6.44 nm in the temperature range studied. The point of maximum stability (minimum integral entropy) ranged between 7.56 and 7.63 kg H_2O per 100 kg of dry solids (d.s.) (water activity of 0.34–0.53). Enthalpy–entropy compensation for the mucilage showed two isokinetic temperatures: (i) one occurring at low moisture contents (0–7.56 kg H_2O per 100 kg d.s.), controlled by changes in water entropy; and (ii) another happening in the moisture interval of 7.56–24 kg H_2O per 100 kg d.s. and was enthalpy driven. The glass transition temperature T_g of the mucilage fluctuated between 42.93 and 57.93 °C.

1. Introduction

Chia (*Salvia hispanica* L.) produces small seeds with oval shape, that have been found to contain many attractive nutritional compounds such as proteins, antioxidants, omega-3 and dietary fiber (Ayerza & Coates, 2005; Ixtaina, Nolasco, & Tomás, 2008; Vázquez-Ovando, Rosado-Rubio, Chel-Guerrero, & Betancur-Ancona, 2009). This has targeted chia seed as an important raw material to obtain functional foods. This has led food scientists and technologists to study several aspects of the seeds as a whole or of components obtained from them. For example, Moreira, Chenlo, Prieto, and Torres (2012) studied the water adsorption isotherms of whole chia seeds and flour, as knowledge of the sorption properties allow to determine adequate moisture content for the drying process and design of equipment related to aeration, storage, and transport.

In the recent years, the demand for hydrocolloids from plant sources has increased because they are the most notable ingredient in liquid and semisolid foods (Koocheki, Reza, & Bostan, 2013). Mucilage and gums are widely used in the food, pharmaceutical and cosmetic industries as thickeners, water retention agents, emulsion stabilizers, suspending agents, binders, coating agents, packing films, etc. When the chia seeds are soaked in water, they exude a clear mucilaginous gel high in uronic acid content that remains tightly bound to the seed (Lin, Daniel, & Whistler, 1994). Chia seed mucilage varies in molecular weight from 0.8 to 2.0×10^6 Da. A tentative structural unit proposed for the polysaccharide is a tetrasaccharide with 4-*O*-methyl-α-D-glucoronopyranosyl residues occurring as branches at *O*-2 of some β-D-xylopyranosyl residues in the main chain consisting of (1 → 4)-β-D-xylopyranosyl-(1 → 4)-α-D-glucopyranosyl-(1 → 4)-β-D-xylopyranosyl units (Lin et al., 1994).

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Segura-Campos, Ciau-Solís, Rosado-Rubio, Chel-Guerrero, and Betancur-Ancona (2014) extracted two gum fractions from chia seeds, one with fat (FCG) and another partly defatted (PDCG). Proximal composition and physicochemical characterization showed these fractions to be different. The PDCG had higher protein, ash, and carbohydrates content than the FCG, in addition to higher water holding (110.5 g water g^{-1}) and water-binding capacities (0.84 g water g^{-1}). The FCG had greater oil-holding capacity (25.7 g oil g^{-1}) and water absorption capacity (44 g water g^{-1}). In dispersion trials, both gum fractions exhibited shear thinning behaviour, although the apparent viscosity of PDCG was higher than that of FCG in the shear rate interval studied. Muñoz, Aguilera, Rodriguez-Turienzo, Cobos, and Diaz (2012a) reported that chia mucilage blended with whey protein concentrates produced films and coatings with improved properties. Srivastava (2014) proposed the use of chia mucilage as a soothing agent in personal care products.

Sorption isotherms data can provide information about the shelf-life stability of a product and used to investigate structural features of a food product, such as specific surface area, pores radius and crystallinity (Pérez-Alonso, Beristain, Lobato-Calleros, Rodríguez-Huezo, & Vernon-Carter, 2006; Spada, Noreña, Marczak, & Tessaro, 2013). The thermodynamics of water vapour sorption as a function of temperature provide a reliable criterion for predicting the storage stability and shelf-life of dehydrated food products. The minimum integral entropy can be interpreted as the required moisture content for forming a monolayer, where the water activity at which a dry food product is most stable (Guadarrama-Lezama et al., 2014), and where strong bonding occurs between the water (adsorbate) and the food (adsorbent) which corresponds to less water being available for chemical and spoilage reactions (Nunes & Rotstein, 1991). On the other hand, it is also important to determine the changes in the physical properties of foods. Glass transition temperature (T_g) can be considered as a critical parameter, since collapse, stickiness, caking, agglomeration problems and re-crystallization phenomena may be avoided in the glassy state of the amorphous matrix (Roos, 1995). In this sense, the T_g can be used, together with moisture content and water activity (a_W), as a reference parameter to characterize properties, quality, stability and safety of food systems (Carter & Schmidt, 2012; Mosquera, Moraga, & Martínez-Navarrete, 2012; Roos, 1995).

The aims of this work were: (a) to study the water adsorption isotherms of the freeze-dried chia mucilage; (b) to evaluate the adsorption process of chia mucilage using differential and integral thermodynamic properties; (c) to establish the most suitable storage conditions (water activity and temperature) by estimating the minimum integral entropy of water vapour molecules adsorbed on the surface of chia mucilage; (d) to determine the driving mechanisms of water vapour adsorption on chia mucilage; and (e) to determine the glass transition temperature of the chia mucilage.

2. Materials and methods

Chia seeds (*Salvia hispanica* L.) were provided by farmers in the region Atlixco, State of Puebla, Mexico. Chemical reagents were purchased from Sigma Aldrich S.A. de C.V. (Toluca, State of Mexico, Mexico). All the water used in the experiments was bidistilled.

2.1. Mucilage extraction

Mucilage extraction was performed according to the method proposed by Muñoz, Cobos, Diaz, and Aguilera (2012b) with some modifications. 40 g of chia seeds were placed in 1 L beaker and bidistilled water was added in a 1:20 weight ratio. The pH was adjusted to 8 using 0.1 M NaOH or HCl solutions. The mixture was stirred with a magnetic stirrer and hydrated for 2 h at a constant temperature of 80 °C. The mucilage was separated from the seed by rubbing the mixture with a rubber spatula over a 40 mesh screen. The filtrate was centrifuged with a Hermle Z323 K highspeed centrifuge (Hermle, Labortechnic, Germany) for 8 min at 524 × *g*. The supernatant was decanted and analysed.

2.2. Freeze–drying

The extracted mucilage was frozen with acetone previously cooled to a temperature of −50 °C using frozen carbon dioxide. Then, the sample was dehydrated using a Labconco Bench Lyph-lock 6 laboratory freeze-dryer (Labconco, MO, USA) for 48 h. Freeze–drying was performed under vacuum conditions at 5 mmHg. Dehydrated products were stored in desiccators above P_2O_5, in order to prevent any increase in absorbed moisture, until required for experiments.

2.3. Sorption isotherms

The adsorption isotherms were determined by the gravimetric method described by Lang, McCune, and Steinberg (1981). Approximately 0.5 g samples of dried mucilage were put into small glass desiccators of 10 cm diameter which contained saturated solutions of different salts that provided water activities (a_W) in the range of 0.11–0.85 (Labuza, Kaanane, & Chen, 1985). Filter paper (Whatman No. 1), placed above the saturated salt solutions, in a perforated plate used as support for the powders and for allowing moisture transmission. Five desiccators of each sample of dried mucilage were placed into forced convection drying ovens at 25, 35 and 40 (±0.1) °C. The samples were weighed with an Ohaus electronic balance (model AP210, Pine Brook, NJ, USA) every five days until equilibrium was achieved. Equilibrium was assumed when the difference between two consecutive weightings was less than 1 mg/g of solids. The time to reach equilibrium varied from 20 to 25 days. The water activity was measured with an Aqualab water activity meter with temperature compensation (model series 3 TE, Decagon Devices, Inc., Pullman, WA, USA). The moisture content of the freeze-dried mucilage was determined by weight difference after vacuum drying (Felisa model FE 100, Mexico City, Mexico) at 60 °C for 24 h, using magnesium perchlorate as a desiccant. All the moisture adsorption experiments were replicated three times. The percentage difference in the equilibrium moisture contents between triplicate samples was, on the average, less than 1% of the mean of the three values. The average values were used in the determination of the moisture adsorption isotherms. The results were adjusted to the GAB (Guggenheim–Anderson–De Boer) model:

$$M = \frac{M_0 C K a_W}{(1 - K a_W)(1 - K a_W + C K a_W)} \quad (1)$$

where M is the equilibrium moisture content (kg per 100 kg of dry solids (d.s.)), M_0 is the moisture content of the monolayer (kg per 100 kg d.s.), C is the Guggenheim constant, and K is the constant correcting properties of the multilayer molecules with respect to the bulk liquid. The parameters were estimated by fitting the mathematical model to the experimental data, using non-linear regression with OriginPro 8 Software (OriginLab Corp., Northampton, MA, USA). Goodness of fit was evaluated using the relative percentage difference between the experimental and predicted values of moisture content, or mean relative deviation modulus (E), defined by the equation. It is generally assumed that a good fit is obtained when $E < 5\%$.

$$E = \frac{100}{n} \sum \frac{|M_1 - M_{Ei}|}{M_i} \quad (2)$$

where M_i is the moisture content at observation i; M_{Ei} is the predicted moisture content at that observation and N is the number of observations (Pérez-Alonso et al., 2006).

2.4. Surface area of sorption

The surface area of sorption (S_0) plays an important role in determining the water bond of a particulate material, and is determined from the monolayer moisture values M_0, as shown in Eq. (3) (Moraes & Pinto, 2012). The moisture content of the monolayer used to calculate the area was obtained from the GAB model.

$$S_0 = M_0 \frac{1}{M_w} N_0 A_{H_2O} = 3.5 \times 10^3 M_0 \quad (3)$$

where M_w is the molecular weight of water (kg mol^{-1}), N_0 is the Avogadro number (6.0×10^{23} molecules mol^{-1}) and A_{H_2O} is the area of a water molecule (1.06×10^{-19} m^2).

The Kelvin equation (Eq. (4)) was used for calculating the critical pore radius. This equation applies primarily in the condensation region of the isotherm (Moraes & Pinto, 2012; Rosa, Moraes, & Pinto, 2010).

$$r_c = \frac{2\sigma V_M}{RT \ln(a_W)} \quad (4)$$

where r_c is the critical radius (m), σ is the surface tension (N m^{-1}), V_M is the molar volume of sorbate (m^3 mol^{-1}), R is the universal gas constant (8.314×10^{-3} kJ mol^{-1} K^{-1}), T is the temperature (K) and a_W is the water activity.

The Helsey equation (Eq. (5)) was used for calculating the adsorbed water multilayer thickness (Singh, Rao, Anjaneyulu, & Patil, 2001)

$$t = 0.354\left(\frac{-5}{\ln a_W}\right)^{1/3} \quad (5)$$

where t is the thickness of the adsorbed water multilayer (nm). Pore radius (r_p) may be obtained by the sum of the critical radius when the capillary condensation or evaporation occurs, and the multilayer thickness, shown in Eq. (6) (Moraes & Pinto, 2012; Rosa et al., 2010).

$$r_p = r_c + t \quad (6)$$

2.5. Thermodynamic properties (integral enthalpy and integral entropy)

The determination of the integral (enthalpy and entropy) thermodynamic properties, and the water activity–temperature conditions where the freeze-dried mucilage minimum integral entropy occurred, considered as the point of maximum storage stability, was established as indicated by Bonilla, Azuara, Beristain, and Vernon-Carter (2010) and Pérez-Alonso et al. (2006). These authors have provided a thorough description of the procedure followed and equations used for this purpose.

The integral enthalpy was calculated using the Clausius–Clapeyron equation at constant pressure of diffusion or surface potential (Φ) (Nunes and Rotstein, 1991; Hill, Emmet & Joyner, 1951)

$$\left(\frac{\partial \ln a_W}{\partial (1/T)}\right)_{\Phi} = \frac{H_s - H_l}{R} = \frac{(\Delta H_{int})_T}{R} \quad (7)$$

where H_s is integral molar enthalpy of water adsorbed of the mucilage (kJ mol^{-1}), H_l is the partial molar enthalpy of adsorbed water at constant temperature and pressure (kJ mol^{-1}), R is universal gas constant (8.314×10^{-3} kJ mol^{-1} K^{-1}), and $(\Delta H_{int})_T$ is the integral enthalpy at a constant temperature (kJ mol^{-1}). A plot in the form $\ln a_W$ vs $1/T$, for a specific constant pressure of diffusion, $(\Delta H_{int})_T$ is determined from the slope $(-\Delta H_{int})_T/R$.

The pressure of diffusion (Φ) can be determined with the following expressions (Nunes & Rotstein, 1991):

$$\Phi = \mu_{ap} - \mu_a = RT \frac{W_{ap}}{W_v} \int_0^{a_W} M \, d\ln a_W \quad (8)$$

$$\Phi = \alpha_1 T \int_0^{a_W} M \, d\ln a_W \quad (9)$$

where μ_{ap} is the chemical potential of the pure adsorbent; μ_a is the chemical potential of the adsorbent in the condensed phase; W_{ap} is the molecular weight of the adsorbent; W_v is the molecular weight of water; and Φ/α_1 is a constant similar to a process at constant Φ.

Eq. (9) was evaluated stepwise. For $a_W < 0.05$, the computed values of the constant pressure of diffusion at any temperature were determined assuming a linear relationship (Henry's law).

$$M = k_w a_W \quad (10)$$

where k_w was the slope of Eq. (10). When $a_W > 0.05$, the GAB model (Eq. (1)) was used. Therefore, Eqs. (1) and (10) were substituted in Eq. (9), to determine Φ/α_1 by the Runge–Kutta method with the help of the MatLab 2013b Software (Math Works Inc., Natick, MA, USA).

The integral enthalpy was needed to determine the integral entropy associated with the sorption process. The integral entropy was calculated using the following equation:

$$(\Delta S_{int})_T = S_s - S_l = \frac{(\Delta H_{int})_T}{T} - R \ln a_W \quad (11)$$

where $S_s = S/N_1$ is integral entropy of water adsorbed in the mucilage; S_l is the partial molar entropy of adsorbed water at constant temperature and pressure (kJ mol^{-1}), and $(\Delta S_{int})_T$ is the integral entropy at a constant temperature.

2.5.1. Compensation theory

Values for integral enthalpy $(\Delta H_{int})_T$ and integral entropy $(\Delta S_{int})_T$ were correlated with the compensation law:

$$(\Delta H_{int})_T = T_B (\Delta S_{int})_T + \Delta G_B \quad (12)$$

where T_B is the isokinetic temperature with an important physical meaning as it represents the temperature at which all reactions in the series proceed at the same rate and ΔG_B (J mol^{-1}) is the measure of the free energy at T_B. The isokinetic temperature and free energy at T_B were calculated using linear regression. To corroborate the compensation theory, a statistical analysis test was proposed, calculating the mean harmonic temperature (T_{hm}) (Tunç & Duman, 2007; Viganó et al., 2012):

$$T_{hm} = \frac{N}{\sum_{i=1}^{N} (1/T)} \quad (13)$$

where N is the total number of isotherms used. The compensation theory only applies if $T_B \neq T_{hm}$. An approximate confidence interval with a significance level of 0.05 was used to calculate T_B from:

$$T_B = T_B \pm t_{m-2,\alpha/2} \sqrt{\mathrm{Var}(T_B)} \quad (14)$$

where:

$$T_B = \frac{\sum \left((\Delta H_{int})_T - \left(\overline{\Delta H_{int}}\right)_T\right)\left((\Delta S_{int})_T - \left(\overline{\Delta S_{int}}\right)_T\right)}{\sum \left((\Delta S_{int})_T - \left(\overline{\Delta S_{int}}\right)_T\right)^2} \quad (15)$$

$$\mathrm{Var}(T_B) = \frac{\sum((\Delta H_{\mathrm{int}})_T - \Delta G_B - T_B(\Delta S_{\mathrm{int}})_T)^2}{(m-2)\sum\left((\Delta S_{\mathrm{int}})_T - \left(\overline{\Delta S_{\mathrm{int}}}\right)_T\right)^2} \quad (16)$$

and m is the number of $((\Delta H_{\mathrm{int}})_T, (\Delta S_{\mathrm{int}})_T)$ data pairs; $\left(\overline{\Delta H_{\mathrm{int}}}\right)_T$ is the average integral enthalpy, and $\left(\overline{\Delta S_{\mathrm{int}}}\right)_T$ is the average integral entropy.

2.6. Glass transition temperature (T_g)

The glass transition temperature was determined by differential scanning calorimetry in a TA-DSC Q1000 calorimeter (TA-Instruments, New Castle, DE, USA) equipped with a mechanical refrigeration system (RCS-refrigerated cooling accessory). Two milligrams of dried chia mucilage equilibrated at different water activities in the range of the 0.11–0.85 and temperatures (25, 35 and 40 °C) were heated in aluminium hermetic pans. Depending on the water activity, the thermal program consisted in a two cycle-scan model, with the temperature ranging from −50 to 150 °C using a heating ramp of 2 °C min^{-1}. An empty aluminium hermetic pan was used as a reference. The DSC was calibrated for temperature using indium, and distilled water standards. The instrument was purged with nitrogen at a flow rate of 100 cm^3 min^{-1}. The data was analysed using Universal Analysis 2000 software, version 4.7a (TA Instruments, New Castle, USA). The glass transition temperature (T_g) was taken as the midpoint of the baseline shift in the second scan obtained in DSC. All measurements were made by triplicate.

The plasticizing effect of water on the glass transition temperature was described by the Gordon–Taylor model:

$$T_g = \frac{X_s T_{g(as)} + kX_w T_{g(w)}}{X_s + kX_w} \quad (17)$$

$$X_s = 1 - X_w \quad (18)$$

where T_g, $T_{g(as)}$, and $T_{g(w)}$ are the glass transition temperatures of the sample, the mucilage at zero moisture content, and water, respectively; X_s is the mass fraction of mucilage (g water/g mucilage), X_w is the mass fraction of water (g water per g mucilage) and k is the Gordon–Taylor parameter, which from the thermodynamic standpoint is equivalent to the ratio of the change of component sample specific heat at their T_g (Couchman & Karaz, 1978). Glass transition temperature of pure water was taken as $T_{g(w)} = -135$ °C (Moraga, Talens, Moraga, & Martínez-Navarrete, 2011).

2.7. Scanning electron microscopy analysis

A JSM-7600F model scanning electron microscope (Jeol Co. Ltd., Tokyo, Japan) with the GB-H mode at 2 kV accelerating voltage was used to investigate the microstructural properties of the freeze-dried mucilage samples stored at the range of temperatures and water activities used for constructing the sorption isotherms. The samples were mounted on carbon sample holders using double-side sticky tape. Micrographs at 250× magnification are presented. Samples were not metalized since the microscopy equipment operates under ultra-vacuum conditions.

2.8. Statistical analyses

The experimental data were analysed using one-way analysis of variance (ANOVA), and Tukey's test used for establishing the statistical significance ($P \leq 0.05$), with the help of the SPSS Statistics 19.0 software package. All experiments were done in triplicate.

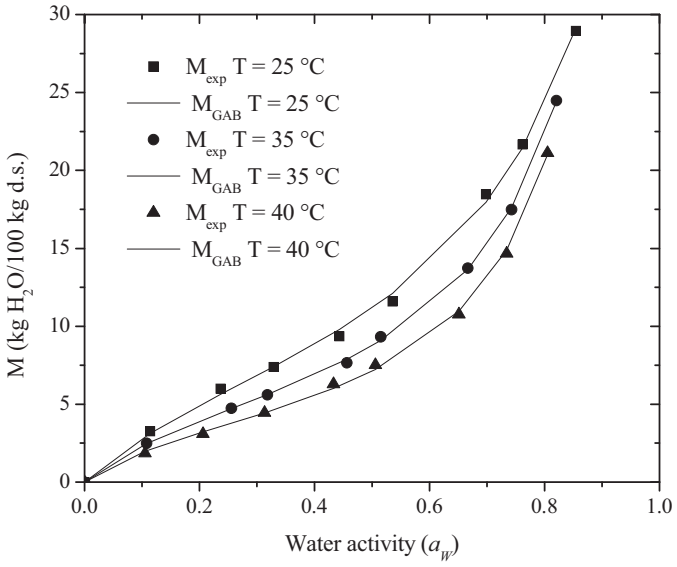

Fig. 1. Water sorption isotherms of freeze-dried chia mucilage.

3. Results and discussion

3.1. Sorption isotherms

The experimental sorption isotherms at 25, 35 and 40 °C for freeze-dried chia mucilage are shown in Fig. 1. They had typical type II sigmoid shape according to Brunauer's classification (Brunauer, Emmett, & Teller, 1938), which is characteristic of biopolymers as potato starch (Viollaz & Rovedo, 1999), gum Arabic and mesquite gum (Pérez-Alonso et al., 2006), *Opuntia* sp. (nopal) mucilage (León-Martínez, Méndez-Lagunas, & Rodríguez-Ramírez, 2010), and chitosan (Rosa et al., 2010).

The experimental sorption data were fitted to GAB model and the model parameters M_0, C and K determined by non-linear regression procedure (Table 1). The mean relative modulus values (E) were less than 3% and the coefficients of determination (r^2) were over 0.998 for all temperatures. The value of the monolayer (M_0) is of particular interest, as it indicates the amount of water that is strongly adsorbed to specific sites and is considered as the optimum value at which a food is more stable (Pérez-Alonso et al., 2006). The values of the monolayer for freeze-dried chia mucilage were in the range of 4.05–7.93 kg H_2O per 100 kg d.s. and decreased as temperature increased from 25 to 40 °C. These results can be attributed to reductions in the number of sites available for water binding due to physicochemical changes, topology and structural changes caused by temperature increases. The parameter C is related to the heat of adsorption of water by the mucilage. It is assumed that strong adsorbent–adsorbate interactions are favoured at lower temperatures, resulting in an increase in C with increasing temperature (Diosady, Rizvi, Cai, & Jagdeo, 1996). In this work the value of C increased with increasing temperature suggesting that interactions between mucilage and water vapour were higher at 25 °C than at

Table 1
Estimated GAB parameters for freeze-dried chia mucilage.

T (°C)	M_0 (kg H_2O/100 kg of dry solids)	C	K	r^2	E (%)
25	7.93 ± 0.20^c	4.966 ± 0.109^a	0.872 ± 0.016^a	0.998	2.97
35	5.33 ± 0.17^b	6.164 ± 0.173^b	0.963 ± 0.024^b	0.999	1.01
40	4.05 ± 0.15^a	6.527 ± 0.241^b	1.010 ± 0.032^b	0.999	2.93

Values are means ± standard error, of three replicates. Superscripts with different letters in same line indicate significant differences ($P \leq 0.05$).

35 °C and 40 °C. Alternatively, it is possible that *C* lacks any physical meaning, and it is the result of mathematical compensation among parameters during the curve-fitting process (Carrillo-Navas et al., 2011).

The values of *K* involve interactions between water molecules and the adsorbent (mucilage) in the multilayer. In this study, *K* values were lower for the freeze-dried mucilage stored at 25 °C, which implies that there were fewer interactions between water molecules and the mucilage in the multilayer. Lewicki (1997) stated that the GAB model describes well sigmoidal-type isotherms when *K* values fall between 0.24 and 1. Also a value of $K \ll 1$ indicates a structured state of the adsorbate in the layers adjacent to the monolayer. For the freeze-dried mucilage, the *K* values at the three temperatures studied fell within this range. The complex nature of adsorption behaviour in food materials is difficult to explain. For biopolymers, the process involves both adsorption and structural changes (crystalline or amorphous) of the polymer matrix because of swelling (Pérez-Alonso et al., 2006). Other factors involved in the mechanism of sorption are porosity and the specificity of water molecule attraction to the surface of hydrophilic sites in biopolymer matrices (Viganó et al., 2012).

Moreira et al. (2012) obtained the experimental sorption isotherms of chia (*Salvia hispanica* L.) seeds of Spain at 20, 35, 50 and 65 °C. The sorption isotherms showed a concurrent increase in equilibrium moisture content with increasing water activity at each temperature. This behaviour followed a typical type II sigmoid shape according to Brunauer's classification (Brunauer et al., 1938). The experimental data were fitted using the GAB model. The monolayer moisture content decreased with increasing temperature, indicating that hygroscopic characteristics occurred at high temperatures. The average monolayer moisture content was 1.9 kg H_2O per 100 kg d.s. The monolayer moisture content values for chia seed were different to those found in this work for the freeze-dried chia mucilage. The values of parameters *C* and *K* also decreased with increasing temperature. The values of *C* ranged between 2.3 and 15, and the values of *K* ranged between 0.923 and 0.948.

3.2. Surface area of sorption

The surface area of sorption values of freeze-dried chia mucilage were calculated by Eq. (3) using the monolayer moisture values obtained from the GAB equation at the temperatures of 25, 35 and 40 °C, resulting in 277.52, 186.44 and 141.69 $m^2\ g^{-1}$, respectively. These results indicate that as temperature increased, the availability of active sites for hydrophilic binding decreased. Such decreasing trends reveal that the binding energies associated with the monolayer and multilayer sorption of water to the mucilage samples decreased with increasing temperature. This can be attributed to a reduction in the total sorption ability of the mucilage, which may in turn reflect temperature-induced physical and chemical modifications (McMinn & Magee, 1999). Labuza (1968) indicated that S_0 values of food products are within the range of 100–250 $m^2\ g^{-1}$. The large sorption surface area of many biopolymers is due to the existence of an intrinsic microporous structure in the biomaterials. The number and size of pores in the carbohydrate matrix determine the total sorption area and the surface properties of pores influences the rate and extent of hydration (Rosa et al., 2010; Singh, Rao, Anjaneyulu, & Patil, 2006). Pore radius (r_p) of freeze-dried chia mucilage was determined according to Eqs. (4)–(6) at different moisture contents and temperatures, and the results are shown in Table 2. These values ranged from 0.87 to 6.44 nm, which according to International Union of Pure and Applied Chemistry (IUPAC) can be classified as micropores (<2 nm) and mesopores (2–50 nm) (Moraes & Pinto, 2012). The pore radius increased as moisture content and temperature increased. Moraes and Pinto (2012) found a similar pore radius range (0.55–8.2 nm) for enzymatic modified paste with 14% hydrolysis degree, and Rosa et al. (2010) found a range of pore radius between 0.51 and 29.7 nm for chitosan. The diffusion mechanisms depend on the properties within the local structure of the porous matrix. In micropores, diffusion is dominated by interactions between the water molecules and the pore walls, i.e., steric and other effects associated with the proximity of the pore walls (entropic effects) become important and barriers control the process. In mesopores, surface forces and capillary forces become important, whereas for the macropores, very little is contributed by the pore characteristics to the adsorption capacity (Azuara & Beristain, 2006; Viganó et al., 2012).

Table 2
Pore radius (nm) of freeze-dried chia mucilage at different moisture contents and temperatures.

M (kg H_2O/100 kg of dry solids)	25 °C	35 °C	40 °C
2.5	0.87 ± 0.01[a]	0.90 ± 0.02[a]	1.00 ± 0.03[b]
5.0	1.17 ± 0.03[a]	1.36 ± 0.04[b]	1.59 ± 0.06[c]
7.5	1.54 ± 0.02[a]	1.85 ± 0.08[b]	2.18 ± 0.08[c]
10.0	1.97 ± 0.06[a]	2.38 ± 0.05[b]	2.77 ± 0.07[c]
12.5	2.47 ± 0.08[a]	2.94 ± 0.10[b]	3.37 ± 0.13[c]
15.0	3.02 ± 0.10[a]	3.54 ± 0.07[b]	3.98 ± 0.11[c]
17.5	3.65 ± 0.12[a]	4.17 ± 0.19[b]	4.59 ± 0.16[c]
20.0	4.34 ± 0.16[a]	4.85 ± 0.21[b]	5.20 ± 0.20[b]
22.5	5.09 ± 0.14[a]	5.55 ± 0.17[ab]	5.82 ± 0.26[b]
25.0	5.90 ± 0.11[a]	6.29 ± 0.19[ab]	6.44 ± 0.24[b]

Values are means ± standard error, of three replicates. Superscripts with different letters in same line indicate significant differences ($P \leq 0.05$).

3.3. Thermodynamic properties (integral enthalpy and integral entropy)

The variation in net equilibrium heat of sorption, or integral enthalpy ($\Delta H)_{int}$, with moisture content indicates the level to which water-solid interaction is greater than the interaction of water molecules. This integral quantity was calculated in a similar manner to the differential enthalpy of sorption, but at a constant pressure of diffusion (Φ). Fig. 2 shows that the net equilibrium heat increased to a maximum with increasing moisture content, and then gradually decreased in magnitude with further increase in moisture content. The mucilage showed a maximum equilibrium heat value of 22 kJ mol^{-1} (approximately) at a moisture content of

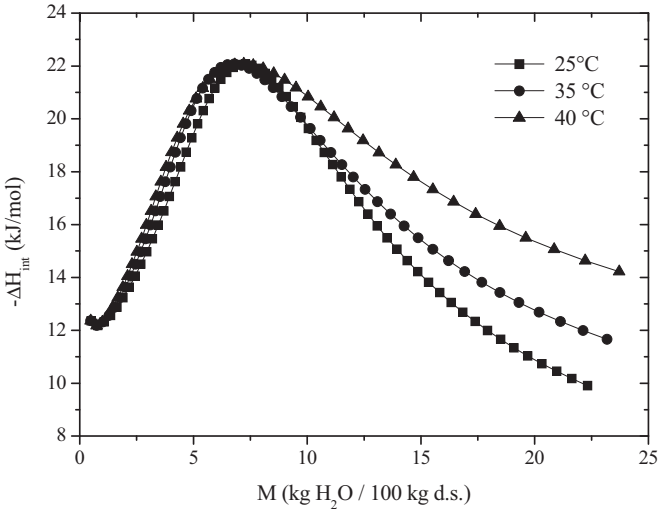

Fig. 2. Integral enthalpy as a function of moisture content of the freeze-dried chia mucilage.

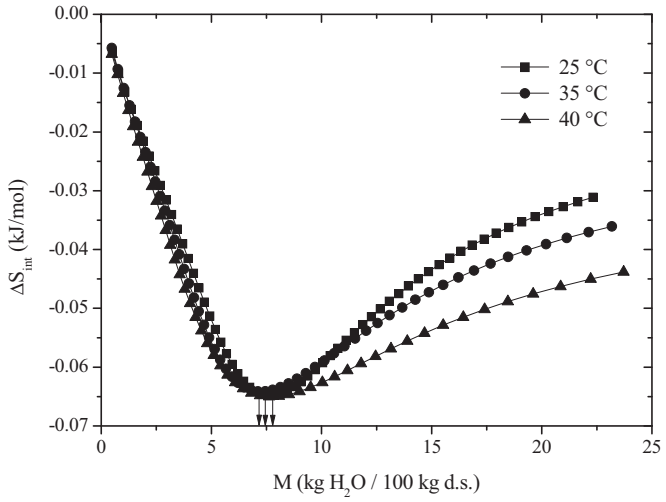

Fig. 3. Integral entropy as a function of moisture content of the freeze-dried chia mucilage.

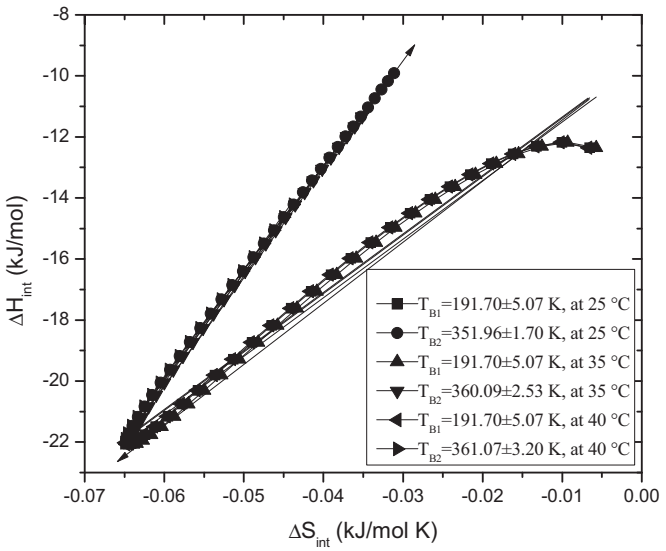

Fig. 4. Integral enthalpy–integral entropy compensation for water sorption in freeze-dried chia mucilage.

7.05 kg H_2O per 100 kg d.s. The low enthalpy values, at low moisture content, are an indication of the occupation of highly accessible sites on the mucilage. However, as the moisture content increased the binding of water at higher energy sites (stronger binding) was reflected in the increase in enthalpy. The maximum enthalpy value indicates the covering of the strongest binding sites and the greatest water–mucilage interaction. The covering of less favourable locations and the formation of multi-layers then follows, as shown by the decrease in enthalpy with increasing moisture content. The magnitude of the enthalpy at high moisture contents reflected the presence of free water (Rizvi & Benado, 1983). Such integral enthalpy data are particularly valuable for estimation of the energy requirement to lower the moisture content of the food product from given initial moisture content to specific final moisture content. A similar relationship between net integral enthalpy and moisture content was reported for potatoes (McMinn & Magee, 2003), freeze-dried yogurts and concentrated yogurts (Azuara & Beristain, 2006), and for pineapple pulp powder produced by different drying methods (Viganó et al., 2012).

Fig. 3 shows the integral entropy as a function of moisture content at 25, 35 and 40 °C. The mucilage showed a decrease in integral entropy reaching a minimum and then increasing in magnitude as moisture content increased. The decrease in integral entropy represents an increase in the restriction of water molecules mobility as available sites become saturated and higher energy sites are utilized; the subsequent increase implies that water molecules are free to form multilayers. At higher moisture contents, entropy will be approximately the same as liquid water (McMinn & Magee, 2003). The minimum integral entropy is considered as that of maximum stability because it is where water molecules achieve a more ordered arrangement within the solid (mucilage) and strong bonds between the adsorbate and the adsorbent occur, thus, water is less available to participate in spoilage reactions (Pérez-Alonso et al., 2006; Bonilla et al., 2010; Viganó et al., 2012). The conditions for maximum stability of mucilage were 7.56 kg H_2O per 100 kg d.s. (a_W = 0.34) at 25 °C, 7.59 kg H_2O per 100 kg d.s. (a_W = 0.41) at 35 °C, and 7.63 kg H_2O per 100 kg d.s. (a_W = 0.53) at 40 °C as can be appreciated in Fig. 3. As temperature increased the moisture content and water activity in the freeze-dried chia mucilage increased. Besides, the integral entropy can be directly related to the order-disorder of water molecules sorbed on food, and therefore is a useful function by which to study the effect of drying method on the stability of the product (Azuara & Beristain, 2006).

3.4. Compensation theory

Enthalpy–entropy compensation theory is used to evaluate physical and chemical phenomena such as sorption reactions. This theory allows one to check whether there will be greater molecular interaction due to freedom reduction or to the link of the molecules in the food, generating larger organization or order (related to enthalpy) over disorganization and greater freedom of the molecules in the food (related to entropy) (Spada et al., 2013). Several authors confirmed the existence of a linear relationship between enthalpy and entropy for water sorption in some foods. Fig. 4 shows the enthalpy–entropy compensation obtained by plotting the integral properties. As can be seen, freeze-dried chia mucilage presented two lines. The first zone at low moisture contents from 0 to 7.56, 7.59 and 7.63 kg H_2O per 100 kg d.s. at 25, 35 and 40 °C, respectively, with $T_{B1} \approx 191.70 \pm 5.07$ K and $\Delta G_{B1} \approx -9.46 \pm 0.22$ kJ mol^{-1} for the three temperatures. The second line covering the rest of the moisture range studied had T_{B2} of 351.96 ± 1.70, 360.09 ± 2.53 and 361.07 ± 3.20 K, ΔG_{B2} of 1.14 ± 0.08, 1.45 ± 0.13 and 1.71 ± 0.18 kJ mol^{-1} for 25, 35 and 40 °C, respectively. These values were obtained by fitting the data with Eq. (9) which presented coefficients of determination (r^2) up to 0.98, indicating that compensation existed. The isokinetic theory can be confirmed because the mean harmonic temperature (T_{hm}) corresponded to 306.35 K, and this value was significantly different from T_B. According to Leffler (1955), it can be postulated that from very low moisture up to values prior to the minimum entropy the sorption process of water molecules is entropy driven ($T_B < T_{hm}$); at the point of minimum entropy, there is an equilibrium between entropy and enthalpy mechanisms; and after minimum integral entropy, enthalpy controls the sorption process of water molecules ($T_B > T_{hm}$). This explains why in this work the sorption process of water molecules was entropy driven at low moisture contents because micropores were predominant and as pores increased to mesopore sizes the process became enthalpy driven. Azuara and Beristain (2006) found similar results for different yogurts and stated that the adsorption process was controlled by entropy when the water molecules were adsorbed in the micropores and was controlled by enthalpy when the water molecules were adsorbed in the mesopores and macropores. From a thermodynamic point of view, the free energy change (ΔG) is an indicative of the affinity water-adsorbent and provide us a criterion to whether water sorption is

a spontaneous ($-\Delta G$) or non-spontaneous ($+\Delta G_B$) process. In this case, the entropic process was spontaneous while enthalpic process was not.

3.5. Glass transition temperature (T_g)

Fig. 5 shows dependence of T_g respect to water activity. T_g decreased as water activity increased, behaviour that can be attributed to the plasticizing effect of water, contributing to the storage and stability of the mucilage and of hydrocolloids in general. The experimental data of T_g of freeze-dried chia mucilage equilibrated at different water activities (0.11–0.85) and temperatures (25, 35 and 40 °C) were adjusted to the Gordon and Taylor model, the coefficients of determination (r^2) were over 0.95 and the mean relative modulus values (E) were less than 3% for all temperatures. The estimated values for T_g were 42.93, 48.78 and 57.93 °C. These values of T_g are consistent with those found for others biopolymers such as the mucilage from *Opuntia* sp. which was of 45 °C for a moisture content of 7.2% d.s. (León-Martínez et al., 2010), gum Arabic (42.6–62.3 °C) between 0.33 to 0.51 of a_W (Righetto & Netto, 2005), maltodextrin solutions (10–25 DE) (45.4 to 54.7 °C) at 32% RH (Cai & Corke, 2000), amylose (43.8 °C). The molecular weight of chia mucilage reported by other researchers ranged from 0.8–2.0 × 10^6 Da (Lin et al., 1994) and this could explain the values of T_g obtained. Glass transition temperature is related to chain stiffness and polymer chain structure; it increases as cross-linking density increases. A lower T_g implies more free volume, presence of shorter chains and more hydrophilic groups causing higher hygroscopicity. Certain physicochemical and structural processes like stickiness, crispness, collapse and the rates of non-enzymatic browning, are correlated to molecular mobility, therefore, these deteriorative processes are related directly to T_g, which determines precisely the critical moisture content of the system where these changes begin to occur. Below this temperature, the amorphous

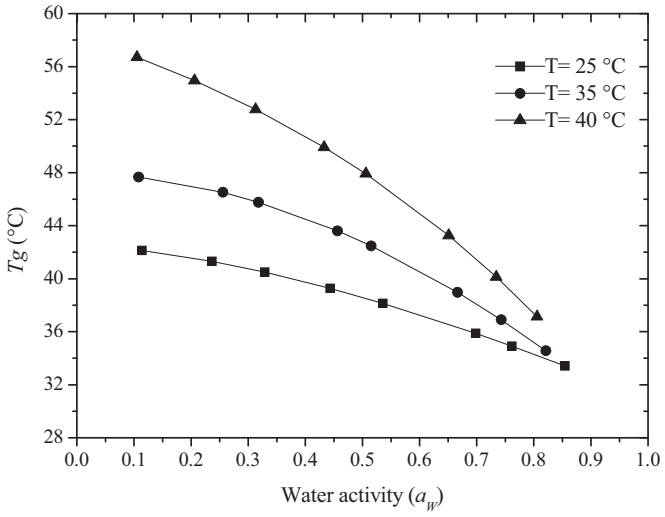

Fig. 5. Effect of a_W on glass transition temperature (T_g) of freeze-dried chia mucilage.

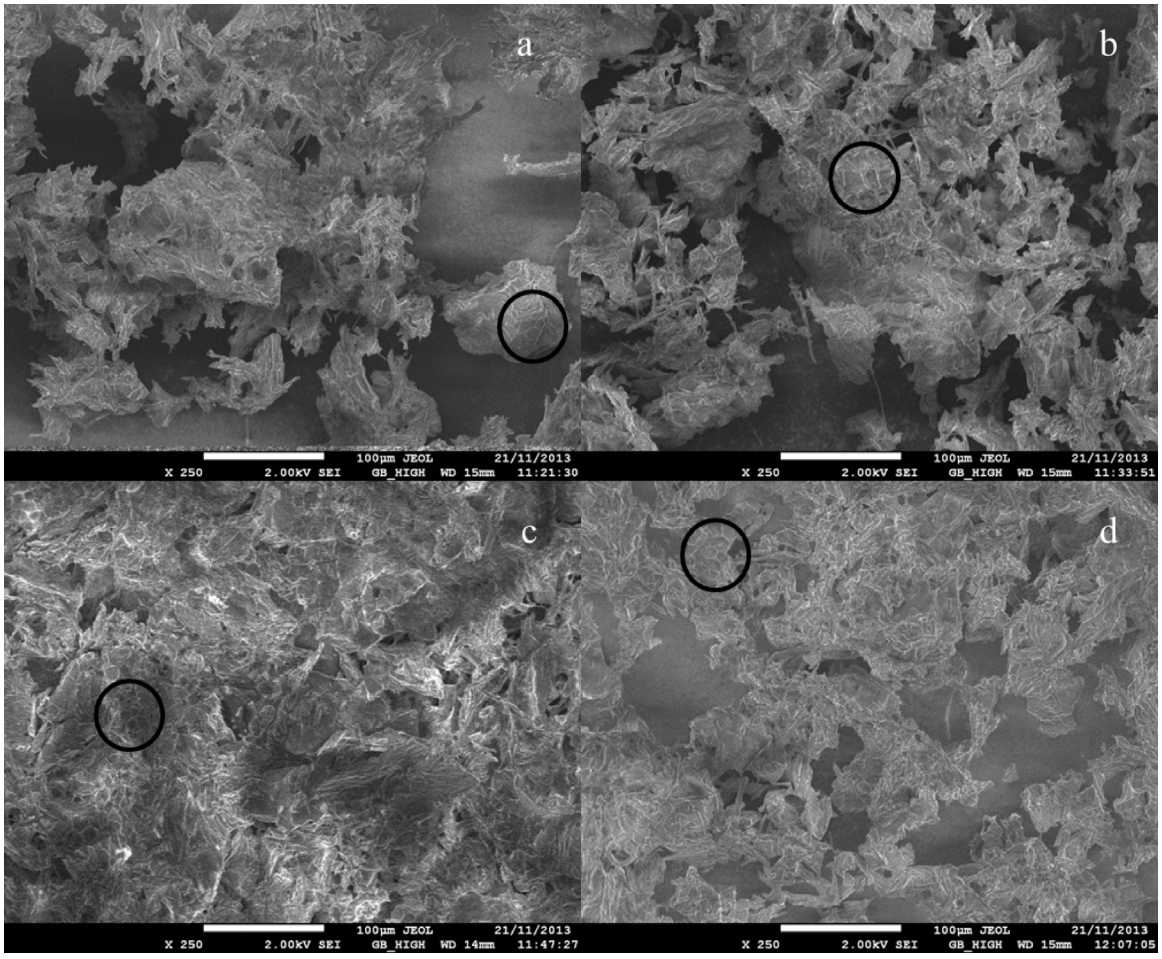

Fig. 6. SEM of freeze-dried chia mucilage at 25 °C and different water activities: (a) 0.115, (b) 0.329, (c) 0.536, (d) 0.765.

materials show a texture from chewy to soft-sticky because the free volume allows less movement of the molecule; this state is called "glassy". On the other hand, in the "rubbery" state (above T_g), the molecules can start wiggling around leading to a soft and flexible material. For example, if we consider a temperature of 70 °C, we could find materials such as maltodextrin or fructans in a glassy state (T_g of 205 and 110 °C, respectively) (Adhikari, Howes, Lecomte, & Bhandari, 2005; Espinosa-Andrews & Urias-Silvas, 2012) but the biopolymers such as chia mucilage or gum Arabic will be in their rubbery state and this would lead to rapid collapse of structure, stickiness and probably to increased rates of deteriorative reactions (Kasapis, 2006; León-Martínez et al., 2010). The results obtained in this work suggest a glassy state of the mucilage in the temperature range studied and at water activities as high as 0.7. Muñoz et al. (2012b) reported that chia mucilage hydration can achieve a water retention of 27 times its weight in water; this result confirms that chia mucilage is stable even at high moisture contents. The values of the estimated parameter k were 0.219, 0.367 and 0.646 at 25, 35 and 40 °C, respectively. The k parameter controls the degree of curvature of the glass transition temperature that dependence on water content and is related to the strength of the interaction between the system components (Gordon & Taylor, 1952).

3.6. Morphology of freeze-dried chia mucilage by scanning electron microscopy (SEM) analysis

SEM micrographs of the freeze-dried chia mucilage at 25 °C and different water activities are shown in Fig. 6. All the samples showed coarse and aggregated amorphous regions with pentagonal structure (pointed out in circles) independently of their water activity. SEM micrographs of the mucilage conditioning at other temperatures (35 and 40 °C) and a_W's showed similar behaviour (not shown here). Therefore, the mucilage appeared to be stable in the range of temperature studied even at high water activity values. The extraction, purification and drying method can significantly affect the microstructure of mucilage. Capitani, Ixtaina, Nolasco, and Tomás (2013) analysed the morphology of the freeze-dried chia mucilage of Argentina describing that it presented a network structure of open pores with appearance of overlapping sheets. León-Martínez et al. (2010) studied the topology of the spray-dried mucilage of *Opuntia* sp. (nopal) from Mexico and observed that it possessed sphere-like agglomerates with collapsed walls, showing structural changes dependent on moisture content.

4. Conclusions

The sorption isotherms of freeze-dried chia mucilage presented a sigmoidal shape, which is characteristic of glassy biopolymers isotherms on water vapour systems. The GAB equation was useful for modelling moisture sorption of the mucilage in a water activity range of 0.11–0.85 and at 25, 35 and 40 °C. The pore radius of freeze-dried chia mucilage presented increasing values in the range from 0.87 to 6.44 nm as moisture content and temperature increased, so that they were considered as micropores and mesopores. The minimum integral entropy established of the most suitable conditions for storage. These conditions included a water activity in the range of 0.34–0.53 for the temperature range between 25 and 40 °C. The enthalpy–entropy compensation theory suggests that the adsorption processes in the mucilage were entropy driven at low moisture contents below the minimum integral entropy onset, after which the sorption process was enthalpy driven. The glass transition temperature T_g of the mucilage was found between 42.93 and 57.93 °C, suggesting that the biopolymer was in an amorphous glassy state even at water activity values as high as 0.7. According to the micrographs obtained, the mucilage appeared to be stable in the range of temperatures studied even at high values of water activity. These chia mucilage properties indicate that it could be used spray-drying microencapsulation different bioactive materials providing them protection against deleterious environmental factors and prolonged shelf-life, when stored under conditions the temperature and water activity conditions determined in this study.

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