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Moisture sorption properties and glass transition temperature of a non-conventional exudate gum (*Prosopis alba*) from northeast Argentine

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ABSTRACT

Water-solid interactions were explored in purified and freeze-dried Prosopis alba exudate gum as approach to get a deeper insight of structural and functional aspects of this novel biomaterial. Particularly, the study of water-binding properties combined with glass transition temperatures allowed obtaining interesting theoretical data for practical applications. The Guggenheim–Anderson–de Boer (GAB) and Generalized D´Arcy and Watt (GDW) models were applied to describe the sorption behavior and thermodynamic properties of the studied gum. The study of the relationship between relative humidity, water content and thermal transitions allowed to characterize the material in terms of water plasticizing susceptibility as well as define the suitable storage conditions that guarantee the quality, safety and physical stability of *P. alba* gum. Obtained results contribute to the characterization of a non-conventional exudate gum with great potential for its use in different food industry applications.

Keywords:

- *Prosopis alba*
- moisture sorption isotherms
- differential scanning calorimetry
- glass transition
- plasticization
- state diagram

1. Introduction

The study of water-solid interactions in low moisture food systems provides useful information that integrates composition and structural features with physical stability and functional properties of food materials (Alpizar-Reyes et al., 2017; Velázquez-Gutiérrez et al., 2015).

Moisture sorption isotherms were widely used as a classical approach to describe the relationship between moisture content and water activity (a_w) of food components at a defined temperature, allowing to select the appropriate conditions of drying, mixing, packaging, and storage (Muzaffar & Kumar, 2016; Polachini, Betiol, Lopes-Filho, & Telis-Romero, 2016). Useful parameters can be obtained from the modeling of experimental sorption data (Al-Ghamdi, Hong, Qu, & Sablani, 2019). With this purpose, several models based on empirical and theoretical criteria have been employed. The Guggenheim–Anderson–de Boer (GAB) model (Anderson, 1946; De Boer, 1953; Guggenheim, 1966) is the most extensively used model to describe the moisture sorption behavior of many foods and biological materials through the entire range of water activity (Polachini et al., 2016). GAB model appears to have many advantages over others, such as having a viable theoretical background since it is a refinement of Langmuir and Brunauer–Emmett–Teller (BET) theories of physical adsorption (Brunauer, Emmett, & Teller, 1938), and the involved parameters have physical meaning (Torres, Moreira, Chenlo, & Vázquez, 2012). More recently applied to food science, the Generalized D´Arcy and Watt model (GDW) (Furmaniak, Terzyk, & Gauden, 2007), has been proposed as a complementary approach to get a deeper insight into the mechanism of water sorption on foodstuff (Furmaniak, Terzyk, & Gauden, 2011). This model assumes the existence of primary sorption centers on the solid surface, where the Langmuir sorption mechanism occurs (Furmaniak, Terzyk, Gauden, & Rychlicki, 2007). Water molecules bonded to those centers may become partially or entirely into secondary sites, as well as one water molecule attached to

primary site may create more than one secondary adsorption site (Furmaniak, Terzyk, Gołembiewski, Gauden, & Czepirski, 2009).

Additionally, the thermodynamic analysis of water sorption in dried foodstuffs performed at different temperatures, has drawn interest because it provides a more thorough interpretation of the sorption mechanism based on energy changes related to degree of binding water on dried products (Alpizar-Reyes et al., 2017; Pérez-Alonso, Beristain, Lobato-Calleros, Rodríguez-Huezo, & Vernon-Carter, 2006).

Linked to moisture sorption phenomena, the analysis of glass transition temperature (T_g) allows a better understanding of the properties, quality, stability and safety of food systems based on the relationship between water content and matrix structure (Velázquez-Gutiérrez et al., 2015). The glass transition, understood as the change from a highly viscous amorphous glassy state to a supercooled liquid (or rubbery) state, may be reached by a temperature increase at constant moisture content, or well, by water content increase at constant temperature (Roos, 1993). The identification of the critical temperatures and moisture contents at which amorphous solids undergo evident rheological changes, contribute to the correct definition of the most suitable storage conditions where time-dependent changes, spoilage reactions and structural transformations (stickiness, collapse, crystallization, and so on) are prevented (Tonon et al., 2009).

Applied to food hydrocolloids, the analysis of water sorption and glass transition was performed to get a better knowledge of the moisture-binding properties, structural features (as interfacial area and pore sizes) (Alpizar-Reyes et al., 2017), optimal conditions for storage (Torres et al., 2012), changes in physical properties (Velázquez-Gutiérrez et al., 2015). The study of the interactions between water and matrix structure, also contribute to assess the hydrocolloids potential functionality as drying aids (Fongin, Kawai, Harnkarnsujarit, & Hagura, 2017; Tonon et al., 2009) or for its use as wall materials for encapsulation (Pérez-Alonso et al., 2006), where gums, proteins,

and starches, among others, play role in reducing the susceptibility to stickiness, caking, collapse and solute crystallization of food powders (Pacheco et al., 2019).

Prosopis alba exudate gum, obtained from South American “Algarrobo blanco” (*P. alba*) tree, was recently reported as a non-conventional hydrocolloid with interesting properties for food industry. *P. alba* exudate gum is mainly composed by carbohydrates (90.19 % db., where reducing sugars represent a 3.40 % db.), protein (13.26 % db.) and inorganic matter (2.29 % db.), and minor components as polyphenols (5.88 mg gallic acid eq./g gum db.) and tannins (2.20 mg tannic acid eq./g gum db.) (Vasile et al., 2019). This gum was described as a complex mixture of high and low molecular weight sugars (*Ara*: 0.67; *Gal*: 0.19; *Rha*: 0.01, *GlcUA*: 0.12) (Vasile, Judis, & Mazzobre, 2017), rendering structural properties ($[\eta]$=1.77·10^{-2} Lg^{-1}; Mv=7.98·10^{5} Da; ζ-potential (2% w/v)= - 43.50 mV), similar to those reported for arabic gum (López-Franco et al., 2012; Vasile, Martinez, Pizones Ruiz-Henestrosa, Judis, & Mazzobre, 2016). The higher protein content in comparison with other exudate gums, largely explains its better functional properties as emulsifier (Vasile et al., 2016) and encapsulant agent (Vasile et al., 2017).

In this context, the aim of present work was to contribute to the knowledge of this interesting gum with important physical aspects such as water sorption properties and thermal behavior of the purified freeze-dried gum.

2. Material and methods

2.1. Extraction and purification processes

Prosopis alba exudate gum was hand collected from trees located in the northeast region of Argentina. The trees were botanically identified by the IBONE (Botanical Institute of Northeast Argentina). The sample included natural exudations (on the main trunk and branches) and exudations produced by mechanical damages (due to agricultural practices and other wounds). The sample had a bitter taste, slightly sweet odor and variable colors (from clear amber to dark reddish brown). The gum was suspended in water (20 % w/v) at 75 ºC under constant stirring for 1 h. The suspension was then clarified by filtration (Whatman No. 4, Uppsala Sweden), dialyzed (MWCO 10 kDA) against distilled water for 24 h with successive water changes, and the resultant solution was frozen at -40 ºC and freeze-dried (Rificor, Model L-I-E300-CRT, Buenos Aires, Argentina).

2.2. Moisture sorption isotherms of purified freeze-dried *P. alba* exudate gum

Water sorption isotherms of purified *P. alba* exudate gum (G) were determined by the static gravimetric method at 25 °C. Samples of about 100 mg of freshly freeze-dried gum were placed in triplicate, in glass vials of the same size. Vials were set in separate hermetic desiccators containing oversaturated salt solutions in the range from 0.11 to 0.90 of water activity according to reported by Greenspan (1977). The desiccators were kept in temperature-controlled chambers at 10, 25 and 35 °C. Samples weight was periodically monitored until reaching equilibrium (weight differences less than ± 0.001 g). The required period for equilibration was about 4 weeks. The equilibrium water content was determined by drying at 105 °C until constant weight, and expressed as g water/ g gum db.

2.3. Sorption isotherms models

The sorption data were fitted to Guggenheim–Anderson–de Boer (GAB) model (Anderson, 1946; De Boer, 1953; Guggenheim, 1966) (Eq. 1) and to the Generalized D´Arcy and Watt (GDW) model (Furmaniak, Terzyk, & Gauden, 2007) (Eq. 2), defined as:

$$Me = \frac{m_o C K a_w}{(1 - K a_w)(1 - K a_w + C K a_w)} \quad (1)$$

$$Me = \frac{m K' a_w}{(1 + K' a_w)} \cdot \frac{1 - k(1 - w) a_w}{1 - k a_w} \quad (2)$$

where *Me* is the equilibrium moisture content (g water/ g gum db.); m_o is the monolayer moisture content (g water/ g gum db.); *C* is the Guggenheim constant; *K* is the constant correcting properties of the multilayer molecules; *m* is the maximum sorption value on primary centers (equal to their concentration); *K´* and *k* are the kinetic constants related to sorption on primary and secondary centers and *w* is the parameter determining the ratio of molecules bonded to primary centers and converted into the secondary ones.

The GAB and GDW parameters were estimated by fitting the mathematical models to the experimental data, using non-linear regression with GraphPad Version 4 (GraphPad, Software Inc., San Diego, CA, USA). The suitability of models was assessed using the determination coefficient (R^2), the standard error of estimate (SEE), and the mean relative deviation modulus (E). The SEE, indicates the fitting ability of a model to a data set. The lower SEE value, the better is the fitting model ability. SEE is defined as:

$$SEE = \sqrt{\frac{\Sigma (M_i - M_{Ei})^2}{df}} \quad (3)$$

where M_i is the moisture content at *i*-th observation (g water/ g gum db.); M_{Ei} is the predicted moisture content at the same observation, *df* is the degree of freedom (number of data points minus the number of constants in the model). Furthermore, the mean relative deviation modulus (E) is the relative percentage difference between the experimental and predicted values of moisture content and is defined as:

$$E = \frac{100\%}{n}\sum\frac{|M_i - M_{Ei}|}{M_i} \quad (4)$$

where *n* is the number of observations. It is generally assumed that an E value below 5 % is indicative of a good fit for practical applications (Alpizar-Reyes et al., 2017).

2.4. Thermodynamic sorption parameters

Thermodynamic parameters were obtained from multi temperature sorption study. The net isosteric heat of sorption or net differential enthalpy (q_{st}) can be used to estimate the energy requirements for the dehydration processes. Estimation of q_{st} (kJ/mol) at constant moisture content can be performed using the Clausius–Clapeyron equation (Pérez-Alonso et al., 2006):

$$q_{st} = -R\left[\frac{d(lna_w)}{d(1/T)}\right]_m \quad (5)$$

where T is the absolute temperature (K), a_w is the water activity and R is the universal gas constant (8.314 J/mol K). $q_{st\ value}$ is obtained from the slope of the curve that resulted from:

$$\ln a_w = \frac{q_{st}}{RT} - \frac{S_d}{R} \quad (6)$$

where S_d (J/mol·K) is the differential entropy of adsorbed water, and it is proportional to the number of available sorption sites corresponding to a specific energy level (Torres et al., 2012).

2.5. Glass transition and water plasticization effect

Differential scanning calorimetry analysis (DSC) were performed for achieving the glass transition temperature of the freeze-dried gum at different water contents. A Mettler Toledo DSC equipment (TA 4000, Columbus, Ohio, USA) with TC11 TA processor and GraphWare TA72 thermal analysis software) was used for thermal studies. The samples (10 – 15 mg) were heated in hermetic aluminum pans at a rate of 10 ºC min^{-1} from −100 to 200 ºC (dynamic method). Glass transition temperatures were determined as the onset point of the step change on the heat flow curve as described in Mazzobre, Buera and Chirife (1997). All measurements were made at least in duplicate.

Experimental T_g-water content curve was fitted with the known Gordon and Taylor (1952) model, considering the onset temperature of the transition:

$$T_{g\,mix} = \frac{w_s T_{gs} + k_{GT} w_w T_{gw}}{w_s + k_{GT} w_w} \quad (7)$$

where w_s is the solid mass fraction, w_w is the water mass fraction, T_{gs} is the anhydrous-solid glass transition temperature and T_{gw} is the amorphous-water glass transition temperature (-135ºC) (Syamaladevi, Sablani, Tang, Powers, & Swanson, 2010), $T_{g\,mix}$ is the glass transition temperature of the system, and k_{GT} is the Gordon and Taylor constant.

Additionally, the curve T_g-a_w was fitted with the Khalloufi (2000) equation:

$$T_g = \frac{Aa_w^2 + Ba_w + T_{gs}}{\alpha a_w^2 + \beta a_w + 1} \quad (8)$$

$$A = T_{gs}K^2(1 - C) \quad (9)$$

$$B = K[T_{gs}(C - 2) + Cm_oT_{gw}k_{GT}] \quad (10)$$

$$\alpha = K^2(1 - C) \quad (11)$$

$$\beta = K[(C - 2) + Cm_ok_{GT}] \quad (12)$$

where T_{gw} is the amorphous-water glass transition temperature (-135 °C); *K, C* and m_o are the GAB parameters (eq. 1); T_{gs} and k_{GT} are derived from Gordon and Taylor (eq. 8) model.

3. Results and discussions

3.1. Water sorption isotherms of *Prosopis alba* exudate gum

Water-solid interactions of purified and freeze-dried *P. alba* exudate gum (G) were evaluated through water sorption behavior. Figure 1 shows the water sorption isotherms obtained for the gum at different temperatures (10, 25 and 35 °C). For all the temperature/relative humidity conditions, the hygroscopic equilibrium was reached after 4 weeks of storage.

Sorption curves showed a sigmoidal shape at the studied temperatures, with a slight increase of the equilibrium water content (*Me*) at low and intermediate a_w range, and a sharp increase of *Me* at a_w higher than 0.8, mainly due to prevailing effect of capillary condensation. This behavior, was identified as isotherm of type II according to Brunauer classification (Brunauer, Deming, Deming, & Teller, 1940), and it is typically attributed to the presence of hydrophilic components like carbohydrates and proteins (Alpizar-Reyes et al., 2017; Muzaffar & Kumar, 2016). As it was previously reported, G is a complex mixture of high and low molecular weight carbohydrates (> 75 % db.), proteins (13.8 % db.) and minerals (2.8 % db.) (Vasile et al., 2016). Thus,

carbohydrates and proteins would be the main responsible of the sorption behavior of the gum. Additionally, the presence of salts even in small proportions, could also have a significant effect on solid-water interactions at low moisture contents (M. Mazzobre, Longinotti, Corti, & Buera, 2001). Similar sorption curves and equilibrium water content values were reported for other exudate gums obtained from botanically related specimens as arabic gum (*Acacia spp.)* (Ramoneda, Ponce-Cevallos, Buera, & Elizalde, 2011) and mesquite gum (*Prosopis spp.)* (Pérez-Alonso et al., 2006), which could be explained considering the similar proximate composition and comparable distribution of acid and ionic groups in the hydrocolloids structure (Torres et al., 2012), typical of this type of gums .

Figure 1 shows that at a certain temperature the equilibrium water content increased with increasing a_w, and also that the *Me* decreased as temperature increased. This trend has been explained considering the excitation state of water molecules. In fact, at high temperatures, the increase in kinetic energy becomes weak the interactions of water molecules with the binding sites of hydrocolloids, promoting a reduction in the water content (Palipane & Driscoll, 1993).

The absence of crossovers or discontinuities in the isotherms, even at the highest temperatures and a_w, could indicate that the high molecular weight polysaccharides in G, governed the sorption behavior. Crossover at high a_w values is characteristic of sugar-rich foods, where the isotherm inversion is caused by sugar dissolution (Cassini, Marczak, & Noreña, 2006). Discontinuities are typically observed in sugar-rich foods due to sugar crystallization. Particularly, the formation of anhydrous sugar crystals promotes the loss of adsorbed water (Syamaladevi et al., 2010). The absence of discontinuities in sorption isotherms of G, evidence the kinetic stability of the amorphous sugars present in the sample. Probably, the high molecular weight carbohydrates and proteins in G prevent crystallization (Mazzobre et al., 2001). The same sorption behavior was reported for other hydrocolloids as carboxymethyl cellulose, guar, locust bean, tragacanth and xanthan gums (Torres et al., 2012), chia

seed mucilage (Velázquez-Gutiérrez et al., 2015), and tamarind seed mucilage (Alpizar-Reyes et al., 2017).

3.2. Sorption models

Experimental sorption data was fitted using the Guggenheim–Anderson–de Boer (GAB) and the Generalized D´Arcy and Watt (GDW) models (Figure 1). The fitting parameters were determined by a non-linear regression analysis and are presented in Tables 1 and 2. The goodness of fit was evaluated using the statistical parameters SEE, E and the R^2, which indicate the fitting ability of models to a data set. Both GAB and GDW models presented low E (<5 %) and high R^2 values, being therefore suitable to describe the sorption behavior of G.

The water content of the monolayer (m_o) obtained from the GAB equation corresponds to the first stage of sorption described by GAB and is of particular interest since it refers to the amount of water adsorbed strongly to primary adsorption sites, it is considered in food as a limit value of stability (Pérez-Alonso et al., 2006b, Rosa et al., 2010).

The GAB model is well recognized for its versatility to evaluate sorption properties in food materials in a wide range of a_w. The GAB monolayer water content (m_o) corresponds to the first shell of water molecules that covers the absorbing surface (Polachini et al., 2016). For the studied gum, the estimated m_o at 25 °C was 0.094 ± 0.005 g water/ g db.. This value was slightly higher than the value reported for arabic gum (0.0811 g water/ g db.) and for mesquite gum (0.0835 g water/ g db.) (Pérez-Alonso et al., 2006) all evaluated at 25 °C. This result indicates that a higher amount of water is required to saturate the surface active sites of the gum. In these conditions, water molecules are strongly adsorbed at specific sites of the material surface, and is considered as the water content affording the most extended period with minimum quality loss at a given temperature (Muzaffar & Kumar, 2016). Thus, in comparison with

the above-mentioned exudate gums (arabic gum and mesquite gum), the freeze-dried G would be more stable at higher water contents.

For G, the monolayer water content showed a slight reduction with the increase in temperature (Table 1), indicating that the availability of specific surface areas for hydrophilic binding decrease with increasing temperature (Rosa, Moraes, & Pinto, 2010). Similar results were reported for mesquite gum and maltodextrin in the temperature range of 25 - 40 °C (Pérez-Alonso et al., 2006), for cassava bagasse in the temperature range 20 - 80 °C (Polachini et al., 2016), and for chitosan between 20 – 60 °C (Rosa et al., 2010).

The Guggenheim´s constant (*C*) is related to the binding strength of the water molecules to the primary active sites on the product surface (Muzaffar & Kumar, 2016). The *C* value of G varied between 11.51 and 18.89, being within the range reported for other food gums (4.8 – 99.9) (Torres et al., 2012). For G, an increase in temperature conducted to a decrease in *C* and this was also reported for other food hydrocolloids as maltodextrin (Pérez-Alonso et al., 2006), and tamarind seed mucilage (Alpizar-Reyes et al., 2017). This behavior was explained considering that the adsorbent-adsorbate interactions are exothermic, resulting in lower *C* values as temperature increases (Diosady, Rizvi, Cai, & Jagdeo, 1996).

The parameter K is a correction factor which takes into account the multilayer molecules relative to the bulk liquid; when K =1 the molecules beyond the monolayer have the same characteristics as pure water (Muzaffar & Kumar, 2016). At the studied temperatures, *K* parameter for G was in the ranged between 0.75 and 0.81, in agreement with values previously reported for arabic gum which varied from 0.74 to 0.84 (Pérez-Alonso et al., 2006). For the studied gum, the *K* values did not show a clear trend regarding temperature changes.

On the other side, the Generalized D´Arcy and Watt model (GDW) was used to provide complementary data on the water sorption mechanism of G. The parameters obtained from fitting the experimental data to GDW model are shown in Table 2.

The parameter *m* informs about the surface concentration of primary adsorption centers. For G, the *m* value at 25 °C was 0.162 (g water/ g dry solids), and this was comparable to those reported for complex food matrices as semolina (0.1669) (Furmaniak et al., 2009) or pineapple (0.1837) (Furmaniak, Terzyk, Gauden, et al., 2007). Considering the maximum water content of G at 25 °C (0.24 g water/ g dry solids), a value of *m*=0.162 indicates that around two-third of the sorbed water is attached strongly to the primary sorption sites.

The GDW *w* coefficient obtained for G at 25 °C, was less than unity (*w*=0.217) indicating that only a small fraction (~22 %) of water molecules, sorbed on primary sites, become into secondary centers for next water molecules. This indicates the existence of geometrical restrictions for growing up of water clusters due to rough and porous characteristics of the material surface (Furmaniak et al., 2009). This value was similar to those previously reported for other multicomponent food systems as semolina (0.2160) and milk powder (0.2988) (Furmaniak et al., 2009).

The GDW *K´* and *k* parameters obtained for G at 25°C, fell in the range of 0.75 - 182.1 for *K´* and 0.901 - 0.983 for k, as previously reported for other food products by (Furmaniak et al., 2009).

Even though the GDW model lead to good fit of sorption data at each explored temperature (Figure 1), a not defined trend of the parameters obtained at different temperatures was observed (Table 2). Namely, *K´* and *k* parameters were defined as temperature dependent kinetic functions related to the sorption on primary and secondary sorption sites (Furmaniak, Terzyk, Gauden, et al., 2007). However, a no clear temperature effect was observed on these parameters. Similarly, the basic assumptions of the GDW model imply to consider the temperature independence of *m* and *w*, based on its physical meaning (Furmaniak et al., 2009). Nevertheless, the *m* and *w* parameters obtained for G resulted slightly different at 10, 25 and 35 °C. This results differ to those previously proposed by Furmaniak et. al. (Furmaniak, Terzyk, & Gauden, 2007) and may be a consequence of the fitting procedure followed to describe

the sorption data at different temperatures. Namely, Furmaniak and coworkers, who first developed and assessed the GDW model on several foodstuffs, proposed a simultaneous fitting of all isotherms at the different temperatures, based on the differential evolution algorithm (Furmaniak, Terzyk, & Gauden, 2007; Furmaniak et al., 2011; Furmaniak, Terzyk, Gauden, et al., 2007). By this approach, they described the whole branch of adsorption isotherms at explored temperatures, obtaining six best-fit parameters (*m, k, K´, w,* q_k and $Q_{K'}$), where q_k and $Q_{K'}$ are the enthalpies related to *k* and *K´* parameters respectively (Furmaniak, Terzyk, Czepirski, et al., 2007). In the current work, the best-fit GDW parameters (Table 2) were obtained as commonly described for other sorption models (Alpizar-Reyes et al., 2017; Muzaffar & Kumar, 2016), that is from individual fitting of data sets experimentally determined at different temperatures. The obtained results may suggest that the assumptions of GDW model made on multi temperature dependency of parameters may be limited to a determined mathematical procedure.

3.3. Thermodynamic analysis of the sorption isotherms

Thermodynamic analysis of the water sorption isotherms made at different temperatures, allows obtaining thermodynamic functions interesting to deepen the understanding of the water-solid interactions (Polachini et al., 2016). In present study, the net isosteric heat of sorption (q_{st}) and the differential entropy of sorption (S_d) were examined for G, as a function of water content employing the GAB and GDW models at 10, 25 and 35 ° C (Figure 2.A and B). Data obtained from both models led to similar plots, with q_{st} decreasing as water content increases (Figure 2.A). At lower equilibrium water content, high enthalpies of sorption could be explained considering the adsorption of water molecules on highly energy binding sites of the first layer (according to GAB mechanism) or primary centers (according to GDW mechanism) placed on the material surface. In these conditions, the adsorbent-adsorbate

interactions are more significant than the interactions among water molecules (Alpizar-Reyes et al., 2017).

As water content increases (over 0.1 g water / g gum b.s.), the sites available for water sorption are less active, formation of multilayers given by adsorbate-adsorbate interactions prevail and consequently q_{st} decreases. According to Pérez-Alonso et al. (2006), a continuous decrease in q_{st} (without a further maximum) may indicate that the biopolymer does not swell, causing solid-water interactions to be predominant only at very low moisture contents, without evidence of changes in the polymeric structure conform moisture increases. A similar behavior was found for other hydrocolloids including tamarind seed mucilage (Alpizar-Reyes et al., 2017), maltodextrin (Pérez-Alonso et al., 2006) and chitosan (Rosa et al., 2010).

Below 0.1 g water/g gum db., the q_{st} values calculated using the GAB model was slightly higher than those obtained from GDW model, and this was also observed for chickpea and lentil seeds (Furmaniak, Terzyk, Gauden, et al., 2007). According to Furmaniak et al. (2011), the differences observed in the GAB or GDW differential enthalpy plots at low water contents, may be consequence of the lack of experimental data in the range of a_w<0.1, which reduces the predictive ability of sorption models. Despite of these differences, the highest q_{st} values calculated for G were in agreement with those reported for other industrial gums which varied between 10 and 35 kJ/mol (Rosa et al., 2010; Torres et al., 2012), suggesting similar energies associated to the sorption on active sites. Above 0.2 g water/g gum db., q_{st} continue falling reaching values similar to those reported for other hydrocolloids as carboxymethyl cellulose, xanthan gum, among others (Torres et al., 2012). At the highest explored water contents, the values obtained using GAB data were slightly higher than those from GDW.

Additionally, the differential entropy of sorption was also evaluated as a function of water content using GAB and GDW models (Figure 2.B). Both models showed that S_d decreased as water content increased, reaching a minimum after which a further

increase was observed. A similar trend was reported for other exudate gums as arabic and mesquite gum (Pérez-Alonso et al., 2006). As suggested by McMinn and Magee (2003), at this minimum, water molecules are in a more orderly arrangement, strongly linked to the solid sorption sites and consequently less mobile. Thus, the correspondent water content could be compared to the monolayer water content regarding water availability for spoilage reactions (Bonilla, Azuara, Beristain, & Vernon-Carter, 2010). The water content value at which G reached the minimum S_d by means of GAB model (about 0.05 g water/ g gum db.) was slightly lower than that derived from GDW (0.1 g water/ g gum db.). This last value was comparable to the monolayer predicted by GAB for G at 25 °C (0.094 g water/ g gum db.), confirming the maximum adsorbed water content that ensures the stability of the gum. After the minimum S_d value, the marked increase indicate that water molecules are free to build-up multilayers, and S_d values tend to equal that of liquid water (Figure 2.B). At the highest water content, the S_d values obtained using the GDW model were higher than the calculated using GAB data.

3.4. Physical stability of the gum based in glass transition and a_w concepts

In order to evaluate the physical stability of the freeze-dried gum at different water activities, the corresponding DSC thermograms were obtained for achieving the glass transition temperature of the samples (Figure 3.A). The endothermal baseline shift represents the T_g value, at which the material undergoes the transition from a highly viscous vitreous state to a supercooled liquid state characterized by low viscosity and high mobility. The observed step in heat flow stand for to the change in the heat capacity of the material at T_g. Thermograms did not show endo or exothermic peaks related to other transitions in the gum such as crystallization/fusion of water or sugars, proteins denaturation, etc. The absence of freezable water at the highest water contents ($a_w > 0.75$), indicate that water crystallization in G is prevented during freezing previous to DSC analysis. Similar results were found for multicomponent samples as

freeze-dried banana and apple analyzed at different relative humidities (Moraga, Talens, Moraga, & Martínez-Navarrete, 2011).

The impact of water content on T_g values, was described using the Gordon & Taylor model (Gordon & Taylor, 1952). Figure 3.B shows the experimental data and fitting model. The parameters derived from Gordon and Taylor equation, allowed to describe the effect of water on G considering a pseudo-binary (water and solid) system. As expected, the glass transition temperature of the gum, decreased with increasing a_w due to water plasticizing effect on the amorphous phase (Syamaladevi et al., 2010). T_g value of the anhydrous gum was 230 ± 15 ºC, slightly higher than the value reported for arabic gum (125 ± 9 ºC), gelatin (150 ± 20 ºC) (Ramoneda et al., 2011) or maltodextrin (163 ºC) (Fongin et al., 2017). Hydrocolloids with high values of T_{gs} are commonly used to provide structural stability to highly hygroscopic foodstuff. The impact of high molecular weight biopolymers as maltodextrin and arabic gum, among others, on the reduction of stickiness and improvement of the handling and quality properties of fruit powders was previously reported (Fongin et al., 2017; Tonon et al., 2009). The increase of T_g in those formulations, was attributed to an increase in the average molecular weight of compatible compounds present in the systems. In this sense, the high glass transition temperatures observed for *P. alba* gum even at high a_w values (> 50°C at a_w 0.75, Figure 3) may promote its use as stabilizer agent in dehydrated systems.

On the other side, the Gordon and Taylor constant (k_{GT}) calculated for G (5.12 ± 0.56) was slightly higher than the reported for arabic gum (3.6) (Tonon et al., 2009), gelatin (2.5) and maltodextrin (3.7) (Ramoneda et al., 2011). A higher value of k_{GT} suggests that G is more susceptible to water plasticization. That is, a smaller amount of water leads to a greater reduction of T_g. For the studied gum, this was attributed to the presence of highly hygroscopic components, such as low molecular weight sugars and salts.

In order to deepen the study on the effect of gum-water interactions on the physical stability of freeze-dried G during storage, the critical water content (CWC) and critical water activity (CWA), proposed as the limit values at which physical transformations like collapse, stickiness and caking occur, were evaluated by two approaches. Firstly, the Gordon and Taylor equation was used to calculate the limit value of water content at which T_g of the studied gum reach the room temperature (25 ºC) (Tonon et al., 2009). For G, the CWC in mass fraction was 0.2, that is 0.25 g water/ g gum db. The corresponding critical a_w (CWA) was then calculated through GAB or GDW models. For GAB the CWA (0.851) was slightly higher than the CWA value predicted by GDW (0.842). This means that G will be stable at 25 °C if RH is lower than 85 %.

Alternatively, the critical conditions of storage were evaluated using the state diagram (Figure 4.A). This tool proposed by Roos (1993), depicts the T_g and equilibrium moisture content (*Me*) as a function of a_w. The dependency of T_g with a_w was well fitted (R^2=0.992) to Khalloufi equation (eq. 8), which predicts a CWA=0.893 at 25 °C. According to GAB and GDW equations, the corresponding CWC were 0.244 and 0.248, respectively. These values were similar to those calculated from the Gordon and Taylor equation, and they were in agreement with the physical appearance observed for the gum (Figure 4.B). Below a_w= 0.8, G the gum kept its structural integrity and remained visually as a free-flowing and bright powder (glassy state). Above a_w= 0.8 changes in the physical characteristics of the gum were observed, resulting in a caked, collapsed and sticky dark material (supercooled liquid or rubbery state) which is usually coupled with loss of rehydration capacity and quality of the additive, being besides susceptible to microbial spoilage.

4. Conclusions

Water-solid interactions on purified and freeze-dried *Prosopis alba* exudate gum were studied through sorption properties and thermal analysis. The water sorption

behavior of G was similar to gums commonly used in industrial applications. The fitting of the water sorption data of G to the GAB and GDW models, allowed to obtain complementary and useful information, relating the sorption properties of the gum with its compositional and structure features. Monolayer water content derived from GAB model (0.094 ± 0.005 g water/ g db.) was consistent with the water content at which the minimum net integral entropy was verified. The sorption analysis through GDW model, informed the existence of geometric constraints due rough or porous at gum surface, which promote that only a small fraction of the water molecules adsorbed on primary sites converts into secondary adsorption centers. In comparison with gums commonly used as excipients such as arabic gum, the studied *P. alba* gum exhibits a higher T_g, indicating that it could be also employed as a good stabilizer agent in dehydrated systems. Additionally, the combined analysis of T_g–a_w–Me, provided a better knowledge regarding physics and thermodynamics properties of G useful for future applications of this non-conventional exudate gum.

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FIGURE CAPTIONS

Figure 1. Water adsorption isotherms of purified and freeze-dried *Prosopis alba* exudate gum at 10, 25 and 35 °C. Symbols represent the experimental data and solid lines show the fitting to the GAB (A) and GDW (B) models.

Figure 2. Net isosteric heat of sorption (A) and differential entropy (B) of sorption as a function of water content, obtained at 25°C for freeze-dried *Prosopis alba* exudate gum using GAB (solid lines) and GDW (dashed lines) models.

Figure 3. DSC thermograms (A) showing the onset of glass transition temperature (arrows) of *Prosopis alba* exudate gum equilibrated at different water activities, and effect of water mass fraction on T_g (B). Symbols represent the experimental data and solid lines show the fitting to the Gordon and Taylor model.

Figure 4. Glass transition temperature (▲) and equilibrium moisture content (●) vs. a_w for freeze-dried *Prosopis alba* exudate gum (A). Physical appearance of the gum equilibrated at different a_w (B). Kalloufi model (dashed line). GAB model (solid gray line). GDW model (solid black line). Critical water activity (CWA) and critical water content (CWC) that ensure the glass transition occurs at room temperature (25 °C).

Figure 1

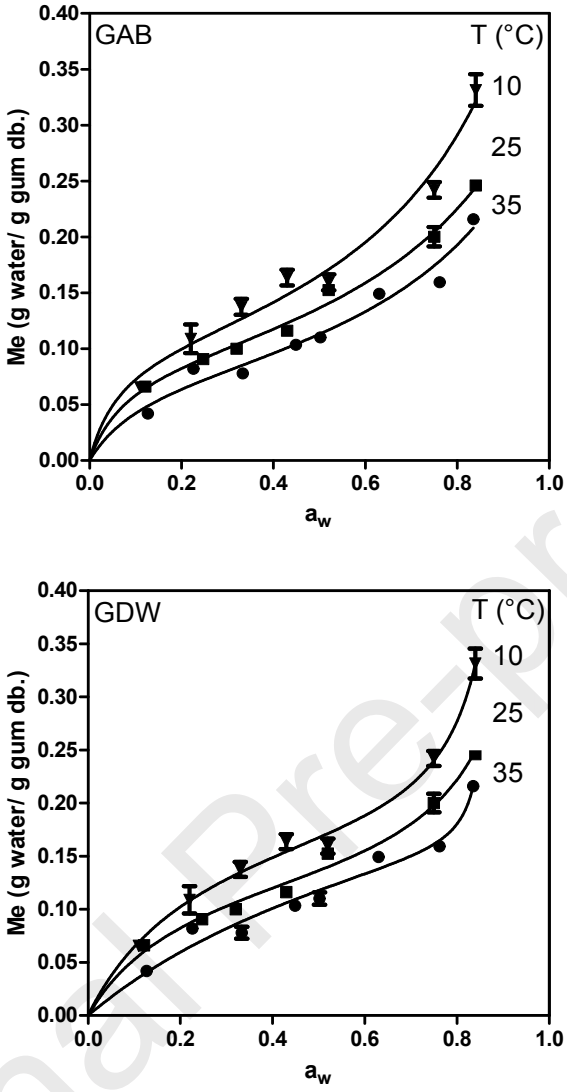


Figure 2

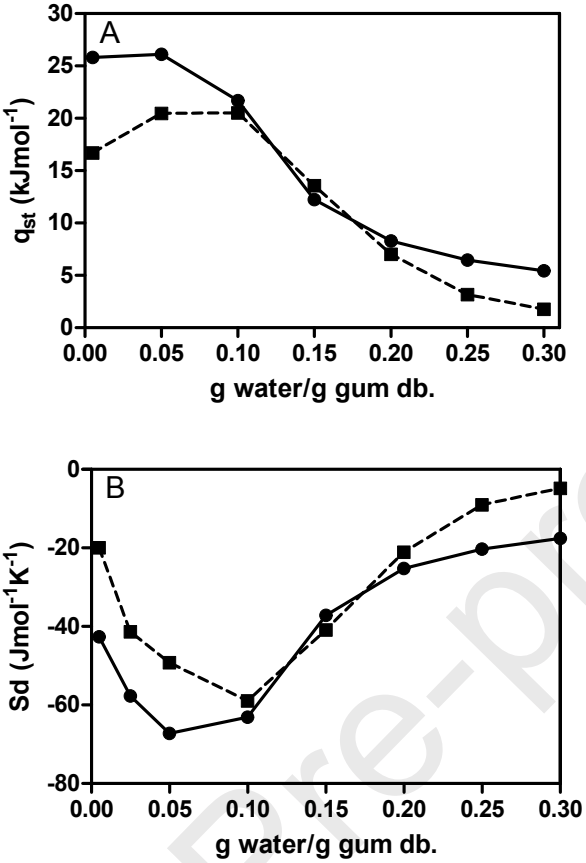


Figure 3

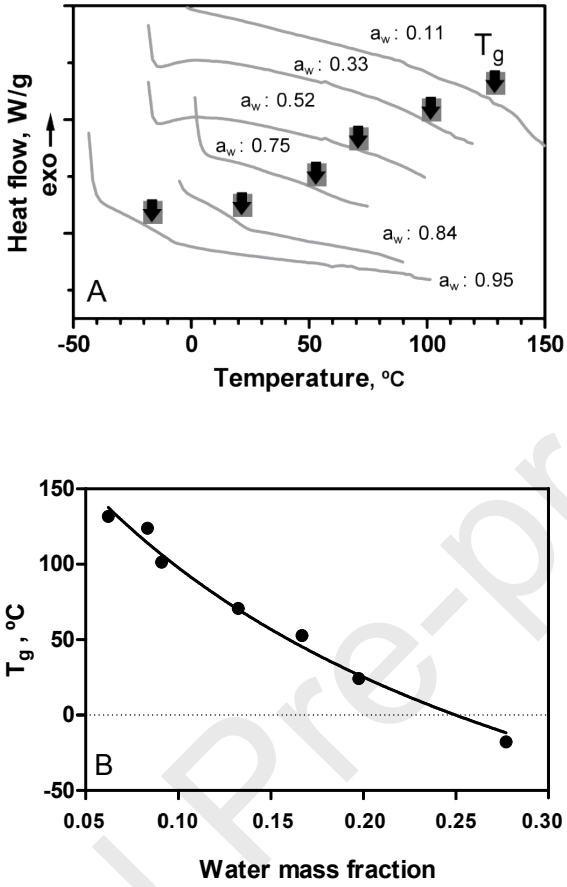


Figure 4

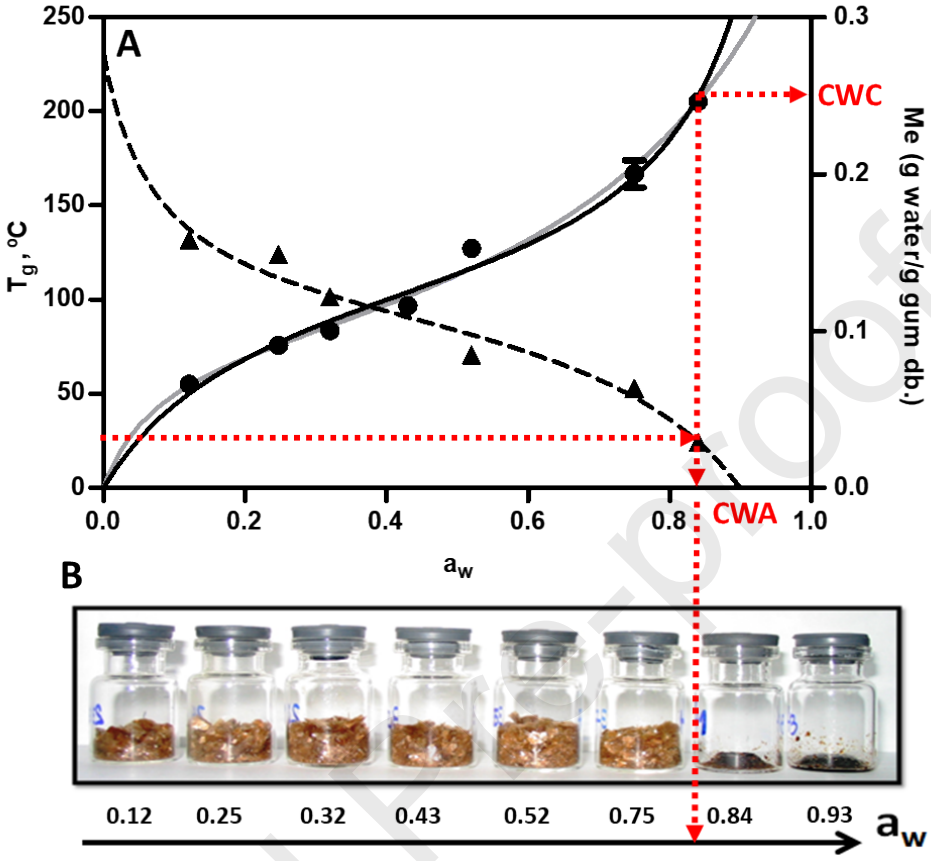


Table 1. Estimated parameters obtained from fitting Guggenheim–Anderson–de Boer (GAB) model to *Prosopis alba* exuded gum water sorption data at 10, 25 and 35 °C. Accuracy of fitting was analyzed considering the correlation coefficient (R^2), the mean relative deviation modulus (E) and the standard error of estimate (SEE).

	Temperature, °C		
Estimated parameters	10	25	35
m_o, g water/g gum db.	0.107	0.094	0.080
C	18.89	16.61	11.51
K	0.805	0.749	0.758
R^2	0.982	0.992	0.971
E, %	4.471	1.647	3.800
SEE	0.017	0.003	0.006

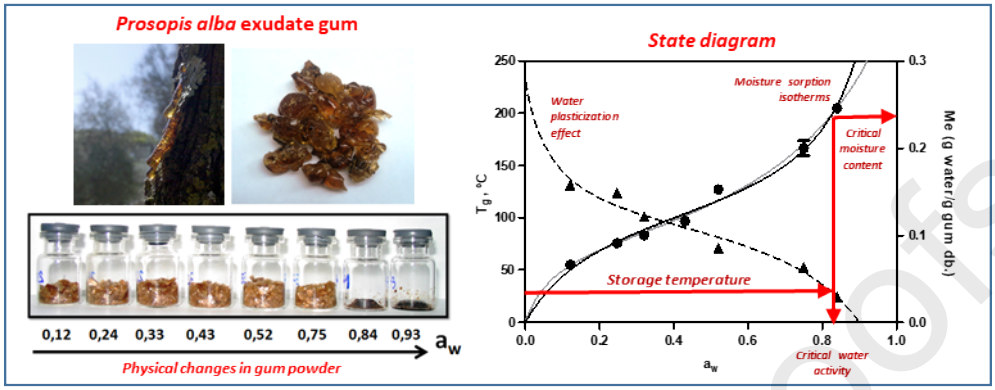
Table 2. Estimated parameters obtained from fitting Generalized D´Arcy and Watt (GDW) model to *Prosopis alba* exuded gum water sorption data at 10, 25 and 35 °C. Accuracy of fitting was analyzed considering the correlation coefficient (R^2), the mean relative deviation modulus (E) and the standard error of estimate (SEE).

	Temperature, °C		
Estimated parameters	10	25	35
m, g water/g gum db.	0.224	0.162	0.306
K´	3.980	4.652	1.201
k	1.066	0.965	1.146
w	0.108	0.217	0.018
R^2	0.993	0.992	0.974
E, %	1.396	0.890	2.728
SEE	0.005	0.003	0.006

Highlights

- Sorption properties of *P. alba* gum were similar to other commercial exudate gums
- GAB and GDW models provided information on compositional and structure features.
- Multi temperature sorption study provides useful thermodynamic functions
- State diagram allowed obtaining the suitable storage conditions of the gum.
- Results extend the potential applications of this currently unused material

Graphical abstract



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María Alicia Judis: Supervision, Visualization, Writing - Review & Editing, Resources, Funding acquisition.

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