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Thermodynamic Properties, Sorption Isotherms and Glass Transition Temperature of Cape Gooseberry (*Physalis peruviana* L.)

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Summary

Adsorption and desorption isotherms of fresh and dried Cape gooseberry (*Physalis peruviana* L.) were determined at three temperatures (20, 40 and 60 °C) using a gravimetric technique. The data obtained were fitted to several models including Guggenheim-Anderson-De Boer (GAB), Brunauer-Emmett-Teller (BET), Henderson, Caurie, Smith, Oswin, Halsey and Iglesias-Chirife. A non-linear least square regression analysis was used to evaluate the models. The Iglesias-Chirife model fitted best the experimental data. Isosteric heat of sorption was also determined from the equilibrium sorption data using the Clausius-Clapeyron equation and was found to decrease exponentially with increasing moisture content. The enthalpy-entropy compensation theory was applied to the sorption isotherms and indicated an enthalpy-controlled sorption process. Glass transition temperature (T_g) of Cape gooseberry was also determined by differential scanning calorimetry and modelled as a function of moisture content with the Gordon-Taylor, the Roos and the Khalloufi models, which proved to be excellent tools for predicting glass transition of Cape gooseberry.

Key words: Cape gooseberry, sorption isotherm, modelling, isosteric heat, glass transition temperature, Gordon-Taylor model

Introduction

Cape gooseberry is a tropical fruit that belongs to the Solanaceae family, genus *Physalis*, a native plant of tropical South America (*1*). Its cultivation today has extended to North America, Europe and Asia. This golden coloured spherical fruit is also known as goldenberry, physalis or uchuva. The berry is enclosed in a papery husk or calyx, has a diameter of around 2 cm and a mass of 4 to 5 g. Its skin is smooth with an orange-yellow colour. The berry has a juicy pulp with numerous small yellowish seeds (*2*) and has been used as a good source of provitamin A, minerals, vitamin C and vitamin B complex. It also contains high levels of antioxidant compounds as well as minerals like phosphorus and iron (*1–4*).

Despite the increasing demand for Cape gooseberry, there is still little information about the application of new processes to improve the shelf life of the fruit, while maintaining its original attributes and minimizing operational costs. One alternative is the dehydration process. In order to optimise the drying or rehydration process from a quality point of view or to guarantee stability of the dried product during storage, the character-

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istics of the sorption behaviour of a product must be known (5). The moisture sorption isotherm describes the relationship between water activity (a_w) and equilibrium moisture content (w_e) of a product at a constant pressure and temperature. Sorption isotherms of many fruits and leaves have been reported in literature (5–8). This is an extremely valuable tool for food scientists and technologists, since it can be used to predict potential changes in food stability, which is relevant in determining the storing method, selecting packaging materials and ingredients as well as designing and optimising drying equipment (9).

Thermodynamic properties such as isosteric heat of sorption during adsorption and desorption processes can be estimated from sorption isotherms. The isosteric heat of sorption is essential to estimate the energy requirement in concentration and dehydration processes and provides important information on the state of water in food products. Water existing in the food is considered as 'bound-water', when the net isosteric heat of sorption reaches the latent heat of vaporisation of water (6). Recently, the concept related to water activity has been enriched with that of glass transition temperature (T_g), thus providing an integrated approach to the role of water in food. Glass transition can be described as a change that occurs in amorphous materials from a high viscosity, glassy state to a low viscosity, rubbery state (10). As T_g is dependent on water content, a change from a rubbery to a glassy state can also occur as a consequence of a decrease in water content during processing or storage. The glass transition supposes drastic changes in some physical properties of the product. It is known that stickiness and collapse of dehydrated powdered products occur due to a strong decrease in viscosity above the T_g (11,12).

The aim of this work is to determine and to model sorption isotherms of Cape gooseberry at three temperatures (20, 40 and 60 °C) and to define relationships of glass transition temperature with water activity and water content. In addition, the net isosteric heat of water sorption, obtained from experimental data, was modelled as a function of moisture content.

Materials and Methods

Raw materials

Cape gooseberry was purchased from a local market in La Serena, Chile. The fruit samples were selected to provide a homogeneous group, based on the date of harvest, colour, size, and freshness according to visual analysis. They were kept refrigerated at 5 °C before drying. Fresh samples of the whole Cape gooseberry were used for determination of the desorption isotherms, while for the adsorption isotherms, the berries were first dehydrated for 12 h at 60 °C and air velocity of 2 m/s in a convective dryer, designed and built at the Department of Food Engineering of University of La Serena, Chile (5). Proximate analysis (moisture, crude protein, lipids, crude fibre and crude ash content) was determined using the AOAC Official Methods (13). Acidity was also determined by AOAC official method (13). The pH value was measured using a potentiometer (Extech Instruments, Microcomputer pH-Vision 246072, Waltham, MA,

USA), and soluble solid content was determined in °Brix using an Abbé refractometer (ATAGO, 1-T, Tokyo, Japan). Water activity was measured at 25 °C by means of a water activity instrument (Novasina, TH-500, Pfäffikon, Switzerland). All analyses were performed in triplicate and expressed in g per 100 g of sample.

Determination of sorption isotherms

Sorption isotherms were determined at 20, 40 and 60 °C. A known mass of sample (in triplicate) was allowed to come into equilibrium with the atmosphere at constant relative humidity inside a hermetically closed flask that contained a glass dish with a saturated salt solution of known water activity as shown in Table 1 (14). The sample mass (15 g) was measured at the start of experiment and at intervals of 20 days until constant mass (±0.0001 g) was reached. Moisture content of the sample was then determined using AOAC official methods (13). This standard gravimetric technique was recommended by The European Cooperative Project COST 90 (15), which deals with physical properties of foods. Thymol was placed separately in a Petri dish inside the flasks with relative humidity above 75 % in order to prevent mould growth (16).

Table 1. Equations to calculate water activity of salt solutions as a function of absolute temperature

Salt	Equation	R^2
LiCl	$\ln a_w = (500.95\ T^{-1}) - 3.85$	0.98
CH$_3$COOK	$\ln a_w = (861.39\ T^{-1}) - 4.33$	0.97
MgCl$_2$	$\ln a_w = (303.35\ T^{-1}) - 2.13$	0.99
K$_2$CO$_3$	$\ln a_w = (145.00\ T^{-1}) - 1.30$	0.97
Mg(NO$_3$)$_2$	$\ln a_w = (356.60\ T^{-1}) - 1.82$	0.99
NaNO$_3$	$\ln a_w = (435.96\ T^{-1}) - 1.88$	1.00
KI	$\ln a_w = (255.90\ T^{-1}) - 1.23$	1.00
NaCl	$\ln a_w = (228.92\ T^{-1}) - 1.04$	0.96
KCl	$\ln a_w = (367.58\ T^{-1}) - 1.39$	0.97
KNO$_2$	$\ln a_w = (244.61\ T^{-1}) - 0.90$	0.90
K$_2$SO$_4$	$\ln a_w = (55.25\ T^{-1}) - 0.21$	0.98

Sorption models and statistical analyses

The analysis of the experimental data obtained for equilibrium moisture content (w_e) and water activity (a_w) at different temperatures was performed using eight mathematical models: Guggenheim-Anderson-De Boer (GAB), Brunauer-Emmett-Teller (BET), Henderson, Caurie, Smith, Oswin, Halsey and Iglesias-Chirife (Eqs. 1–8):

GAB model
$$w_e = \frac{w_m \cdot C \cdot k \cdot a_w}{(1 - k \cdot a_w) \cdot (1 + (C-1) \cdot k \cdot a_w)} \qquad /1/$$

BET model
$$w_e = \frac{w_m \cdot C \cdot a_w}{(1 - a_w) \cdot (1 + (C-1) \cdot a_w)} \qquad /2/$$

Henderson model
$$w_e = 0.01 \left(\frac{-\log(1 - a_w)}{10^B} \right)^{\frac{1}{A}} \qquad /3/$$

Caurie model $\qquad w_e = \exp\left[a_w \cdot \ln(A) - \dfrac{1}{4.5 \cdot w_s}\right]$ /4/

Smith model $\qquad w_e = B + A \cdot \log(1 - a_w)$ /5/

Oswin model $\qquad w_e = A \cdot \left[\dfrac{a_w}{1 - a_w}\right]^B$ /6/

Halsey model $\qquad w_e = \left(\dfrac{A}{\ln(1/a_w)}\right)^{\frac{1}{B}}$ /7/

Iglesias-Chirife model $\qquad w_e = B + A \cdot \left[\dfrac{a_w}{1 - a_w}\right]$ /8/

where w_m is the monolayer water content (g per g of dry matter (dm)), C and k are dimensionless parameters in the GAB and BET equations, a_w is the water activity, A is a dimensionless parameter related to the Henderson, Caurie, Smith, Oswin, Halsey and Iglesias-Chirife models, w_s is the safe storage moisture content (g per g of dm), and B is a dimensionless parameter in the Henderson, Smith, Oswin, Halsey and Iglesias-Chirife models. The eight models used in this study have described correctly the sorption isotherms of agro-food products for a_w values between 0.05 and 0.95 (8,17). The parameters of the mentioned equations were obtained by linear regression analysis using the SigmaPlot v. 11 software (Systat Software Inc., San Jose, CA, USA).

The influence of temperature on the physicochemical parameters (w_m, C, k and w_s) was evaluated using an Arrhenius-type equation (Eq. 9):

$$\psi = \psi_o \cdot \exp\left(\dfrac{-E_a}{RT}\right) \qquad /9/$$

This method allows determination of the activation energy (E_a, kJ/mol), with ψ as the parameter under study, and ψ_o as the Arrhenius factor.

Three parameters were used to evaluate the models correlated to experimental kinetics, namely correlation coefficient (R^2), sum of squared error (SSE) (Eq. 10), and reduced chi-square (χ^2) (Eq. 11):

$$\text{SSE} = \dfrac{1}{N} \sum_{i=1}^{N} (w_{ei} - w_{ci})^2 \qquad /10/$$

$$\chi^2 = \dfrac{\sum_{i=1}^{N} (w_{ei} - w_{ci})^2}{N - m} \qquad /11/$$

where w_{ei} is the experimental moisture content (g per g of dm), w_{ci} is the predicted moisture content (g per g of dm), N is the number of data values, m is the number of constants and i is the number of terms. The lowest values (nearest to zero) for SSE and χ^2, as well as the highest values for R^2 (≥ 0.90), indicate which of the models were the most appropriate. Most authors selected these statistical tests as criteria to evaluate the fit quality of the models (17).

Estimation of thermodynamic properties

The net isoteric heat of sorption is defined as the difference between total isoteric heat of sorption (q) and the heat of vaporisation of pure water (r) (Eq. 12), and can be determined as a function of temperature as shown in Eq. 13:

$$q_n = q - r \qquad /12/$$

$$q_n = -R \cdot \dfrac{\partial(\ln a_w)}{\partial(1/T)} \qquad /13/$$

where a_w is the water activity, q_n is the net isoteric heat of sorption (kJ/mol), R is the universal gas constant (kJ/(mol·K)) and T is the absolute temperature (K). The net isoteric heat of sorption (q_n) is derived from the Clausius-Clapeyron equation, applied to the system and to pure water under the assumption that moisture content of the system remains constant, and r and excess heat of sorption do not change with temperature (18,19). The q_n can be estimated by plotting $\ln a_w$ against $(1/T)$ for selected moisture content of the material, and determining the slope ($-q_n/R$). An empirical exponential model proposed by Tsami (20) was used to relate q_n with equilibrium moisture content, w_e (Eq. 14):

$$q_n = q_o \cdot \exp\left(\dfrac{-w_e}{w_o}\right) \qquad /14/$$

with q_o as the net isoteric heat of sorption of the first molecule of water in the food (kJ/mol) and w_o as a characteristic moisture content of the food material (g per g of dm), at which this net isoteric heat of desorption was reduced by 63 %. The constants q_o and w_o are estimated by fitting Eq. 14 to the values of q_n, obtained by applying Eq. 13 to experimental isotherms. In this work, the net isoteric heat of desorption and adsorption were determined from the estimated sorption isotherms by selecting the model that best fitted the experimental data. The change in molar differential entropy can be calculated from the Gibbs–Helmholtz equation (21) as given in Eq. 15:

$$\Delta S = \dfrac{\Delta H - \Delta G}{T} \qquad /15/$$

where ΔS is the change in specific entropy in J/(mol·K), ΔH is the change in enthalpy in J/mol, and ΔG is the free energy in J/mol calculated by Eq. 16:

$$\Delta G = R \cdot T \cdot \ln a_w \qquad /16/$$

Substituting Eq. 16 in Eq. 15 and rearranging:

$$\ln a_w = \dfrac{\Delta H}{R \cdot T} - \dfrac{\Delta S}{R} \qquad /17/$$

The enthalpy and entropy changes can be calculated from Eq. 17 by plotting the sorption isotherm in the form of $\ln a_w$ *vs.* $1/T$ for values of the material moisture content and then determining the slope ($\Delta H/R$) and the intercept ($-\Delta S/R$).

Measurement of glass transition temperature

Glass transition temperature (T_g) of the Cape gooseberry samples at different moisture contents was determined using a differential scanning calorimeter (DSC;

model DSC823e, Mettler-Toledo, Schwerzenbach, Switzerland) equipped with DSC sensor HSS7. The instrument was calibrated by using indium standard. A mass of berry sample between 10 and 15 mg was placed into a Mettler-Toledo DSC pan (ME-00026763) that was then sealed hermetically. An empty pan was used as reference (air). The sample was first cooled to –50 °C at –5 °C/min, and then scanned from –50 to 80 °C at a rate of 10 °C/min to determine its thermal behaviour. Before scanning the samples, a scan of two empty pans under the same test conditions was conducted to obtain baseline subtraction. T_g was recorded as the middle temperature on the curves of the heat flow *vs.* temperature, where a step change in the heat capacity is evidenced (*10*). STARe software v. 9.1 (Mettler-Toledo) was used to determine midpoint temperatures for DSC glass transition, according to ASTM-IEC standard.

Modelling of glass transition temperature

To predict the plasticisation effect of water, glass transition temperature and moisture content data were fitted to the model proposed by Gordon and Taylor (*22*). The Gordon-Taylor model (Eq. 18) has proved to be a reliable predictor of glass transition temperature of sugars at various water contents and has been used in the case of several fruit and vegetable samples that can be considered as binary mixtures of solids and water (*12*):

$$T_g = \frac{T_{gs} \cdot (1-\omega) + \omega \cdot k \cdot T_{gw}}{(1-\omega) + \omega \cdot k} \qquad /18/$$

where T_g is glass transition temperature (K), T_{gs} is glass transition temperature for anhydrous solids (K), T_{gw} is the glass transition temperature for amorphous water (K), ω is the mass fraction of water (g of water per g of sample) and k is the Gordon-Taylor constant.

The relationship between T_g and a_w was also modelled using two other empirical equations developed by Roos (*23*) (Eq. 19) and Khalloufi *et al.* (*24*) (Eq. 20):

$$T_g = A \cdot a_w + B \qquad /19/$$

$$T_g = \frac{C \cdot a_w{}^2 + D \cdot a_w + E}{c \cdot a_w{}^2 + d \cdot a_w + 1} \qquad /20/$$

In these equations T_g is the glass transition temperature (K) and A, B, C, D, E, c, and d are model parameters.

Results and Discussion

Behaviour of sorption isotherms

Proximate analysis of Cape gooseberry, based on 100 g of fresh product, showed a content of crude protein (N× 6.25) of (1.23±0.15) g, total lipids of (0.35±0.05) g, crude fibre of (2.41±0.17) g, crude ash of (0.77±0.03) g, and available carbohydrates (by difference) of (11.79±0.10) g. Soluble solid content was (13.96±0.16) °Brix, titrimetric acidity (2.01±0.09) g of citric acid per 100 g of fresh product and pH=3.5±0.1. The initial moisture content of the fresh and dried Cape gooseberry samples was (83.45±0.15) and (33.00±0.80) g per 100 g of sample (dried at 60 °C), respectively. These values were comparable in magnitude to those reported by Puente *et al.* (*25*) and Ramadan (*4*).

Sorption isotherms experimentally obtained for Cape gooseberry samples at temperatures of 20, 40 and 60 °C are presented in Fig. 1, where the effect of temperature on the moisture sorption characteristics is observed. The sorption isotherms of Cape gooseberry are typical type I sigmoid curves according to van der Waals classification (*26*). Various authors have reported this behaviour for different foods (*27,28*). Fig. 1 also shows that for water activity (a_w) below 0.85, as expected in an exothermic moisture sorption process, the equilibrium moisture content decreased with increasing temperature at constant value of a_w, indicating that the sugars become less hygroscopic. In addition, since samples absorbed more water at lower temperatures than at higher temperatures, water molecules at lower temperatures have a lower kinetic energy, which is not enough to overcome the corresponding sorption energy (*29*). However, for a_w>0.85 a cross-over of the isotherms with temperature is observed, *i.e.* the equilibrium moisture content increased with temperature for a given a_w value.
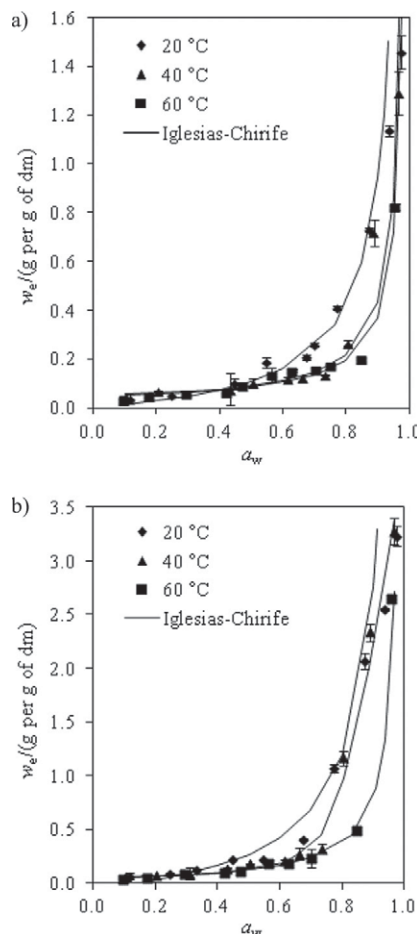

Fig. 1. Experimental *vs.* modelled (Iglesias-Chirife) data for: a) adsorption and b) desorption isotherms of Cape gooseberry at three different temperatures; w_e=equilibrium moisture content, a_w=water activity, dm=dry mass

The nature of the isotherms may be the result of occurrence at low water activities of physical sorption on strongly active sites of proteins and sorption to the surface hydroxyl group of crystalline sugar. Furthermore,

according to Falade and Aworh (*30*) local dissolution of sugar alcohols, swelling of proteins and appearance of new active sites may also occur. In the intermediate a_w range, sorption occurs at less active sites, while at higher water activities, dissolution of sugars gradually takes place, resulting in a complete exudation of sugars in the solution. Sorption isotherm of Cape gooseberry follows the type I behaviour, which is usual for sugar foods, where the Iglesias-Chirife model is the most adequate. This behaviour may also be attributed to the relatively high carbohydrate content of dried Cape gooseberry, similar to that of spray-dried tomatoes (*12*).

For the characterisation of the water sorption of food materials in the water activity range of 0.10–0.95 the GAB equation (Eq. 1) has been recommended (*15*) as the fundamental equation. Table 2 shows the three GAB parameters obtained. The GAB model introduced a second well-differentiated sorption stage for water molecules and an additional energy constant, *k*. The obtained *k* values were, in all series, near to 1.0. As in the BET equation, the monolayer capacity is also represented in one of the three GAB constants. In all sorption series at 20 and 40 °C the monolayer moisture content (w_m) obtained by the GAB model was slightly lower than that obtained by the BET model (Table 2); however, at 60 °C both values tended to equalise. The third parameter, *C*, is also an energy constant known as the BET constant, but with slightly different physical meanings (*31*).

Fig. 1 also indicates that for $a_w > 0.85$ the different isotherms intersect, mainly due to the rise of product moisture content for these water activity values. This could be due to the increase of sugar solubility in the product, a phenomenon that has been demonstrated to occur more frequently in foods rich in sugar (*27*). Another explanation for this type of intersection may be due to a possible increase in enzymatic activity and to intermingling of water molecules, carbohydrates and proteins (*28*).

Furthermore, the isotherms of Cape gooseberry (adsorption and desorption) presented a hysteresis phenomenon for the three temperatures studied, demonstrating that the water adsorption and desorption processes were irreversible. This phenomenon occurred because fresh foods hold more moisture than dried foods over the entire range of a_w, probably due to cell damage occurring in food that has been dehydrated. The hysteresis phenomenon was strongly affected by temperature, as the distance between adsorption and desorption isotherms increased with the change of temperature, showing that the isotherms have a bigger lobule among them at any of the three working temperatures (Fig. 1).

In the field of water vapour sorption by a solid sorbent, moisture sorption hysteresis is the phenomenon by which two different paths exist between the adsorption and desorption isotherms (*16*). The effect of hysteresis on food is important, even though it can be relatively low in magnitude. Rizvi (*32*) stated that the extent of hysteresis is related to the nature and state of the components in a food. It may reflect their structural and conformational rearrangement, which alters the accessibility of energetically favourable polar sites and thus, may hinder the movement of moisture. Iglesias and Chirife (*33*) also recognised that it is not possible to give a single explanation for the hysteresis phenomena in foods, due to food being a complex combination of various constituents, which cannot only sorb water independently but also, interact among themselves. Hysteresis is not fully understood, although there is general agreement that some thermodynamically irreversible processes must occur during desorption or adsorption, or both. The most favoured theory used to explain this thermodynamical peculiarity suggests that under wet conditions water is adsorbed at almost all polar sites in the molecular structure of the material. Upon drying and shrinkage, the molecules and their water holding sites are drawn closely enough together to form a stable structure that has a reduced water holding capacity.

Mathematical modelling of sorption data

In Table 2 the results of the regression analysis of the equations used to model the experimental data of sorption isotherms at 20, 40 and 60 °C are shown. GAB, BET and Caurie models have been used in many food studies, especially due to the interpretation of their parameters w_m and w_s, which are related to the maximum food stability under the process/storage conditions (*16*). Monolayer moisture (w_m) calculated with the GAB model was similar to that calculated with the BET model. The monolayer moisture content obtained by the GAB model for adsorption isotherms was between 0.044 and 0.075 g per g of dm, and for desorption isotherms between 0.075 and 0.136 g per g of dm. Similar values of w_m for the GAB model were reported by other authors; Hossain *et al.* (*34*) reported w_m values between 0.041 and

Table 2. Parameters of proposed models for moisture sorption isotherms of Cape gooseberry at 20, 40 and 60 °C

Models	Parameters	Adsorption			Desorption		
		Temperature/°C					
		20	40	60	20	40	60
GAB	w_m	0.075	0.044	0.053	0.136	0.084	0.075
	C	4.228	56.117	10.424	3.571	7.374	4.678
	k	1.008	1.009	0.954	1.029	1.056	1.012
BET	w_m	0.083	0.049	0.053	0.140	0.093	0.077
	C	3.432	14.165	8.440	3.468	6.105	4.533
Henderson	*A*	0.807	1.441	1.396	0.650	1.265	1.040
	B	−1.503	−1.996	−1.929	−1.486	−2.089	−1.730
Caurie	w_s	0.054	0.055	0.058	0.060	0.068	0.060
	A	71.744	36.675	21.861	121.207	18.107	27.952
Smith	*A*	−0.789	−0.274	−0.234	−0.786	−0.515	−0.419
	B	−0.081	0.016	0.026	−0.004	0.015	0.008
Oswin	*A*	0.140	0.120	0.099	0.240	0.165	0.142
	B	0.721	0.674	0.584	0.750	0.601	0.820
Halsey	*A*	0.092	0.047	0.031	0.230	0.097	0.101
	B	0.961	1.150	1.276	0.756	1.055	0.912
Iglesias-Chirife	*A*	0.104	0.043	0.035	0.311	0.104	0.083
	B	0.002	0.047	0.052	−0.049	0.037	0.038

A, B, C, k=dimensionless parameters
w_m=monolayer water content in g per g of dry matter
w_s=safe storage water content in g per g of dry matter

0.050 g per g of dm of pineapples; Kiranoudis *et al.* (*35*) obtained values between 0.087 and 0.212 g per g of dm of potatoes, carrots, onions, tomatoes and green pepper; Kaymak-Ertekin and Gedik (*27*) showed values from 0.067 to 0.220 g per g of dm of grapes, apricots, apples and potatoes; Talla *et al.* (*17*) found values between 0.080 and 0.185 g per g of dm of banana, mango and pineapples. In this study, values of safe storage moisture content (w_s) predicted by the Caurie model were between 0.054 and 0.058 g per g of dm for the adsorption isotherm and between 0.060 and 0.068 g per g of dm for the desorption isotherm. The GAB model described sigmoid type isotherms and fulfilled the requirement of the BET model when the parameters were kept within the following regions: $0.24 < k \leq 1$ and $5.67 \leq C \leq \infty$. Outside these regions the isotherm is either no longer sigmoidal or the monolayer capacity is estimated with an error greater than ± 15.5 % (*36*). It is worth recalling that the BET model is only valid for $a_w < 0.60$.

Statistical analyses of mathematical models

The results of the statistical analyses applied to the proposed mathematical models for both adsorption and desorption isotherms at the three different temperatures are shown in Table 3. In general, all proposed models gave good fits of the experimental data according to the values of SSE and χ^2, which were quite low and near zero, and R^2 values near unity. As can be seen in Table 3 and taking into account the three statistical tests, the models that best fitted the experimental data for the desorption isotherms ($R^2 \geq 0.97$; SSE≤ 0.077 and $\chi^2 \leq 0.010$), as well as for the adsorption isotherms ($R^2 \geq 0.94$; SSE≤ 0.011 and $\chi^2 \leq 0.014$) were the Smith, Iglesias-Chirife and Halsey models. They also predicted satisfactorily the equilibrium moisture content of Cape gooseberry for the air-drying temperatures between 20 and 60 °C. Moreover, the results are valid for a complete range of water activity from 0.10 to 0.95 for all the models except for the BET equation, which is suitable between $0.10 \leq a_w \leq 0.60$. The goodness of fit for the mentioned mathematical models has been reported by other authors studying sorption behaviour of different foods (*16,17,27,37*). Although the BET model showed satisfactory statistical tests, the range of a_w in which the model can predict sorption behaviour is incomplete, since w_e can be estimated for $a_w < 0.60$; for this reason, only the Iglesias-Chirife model was plotted in Fig. 1 for adsorption and desorption experimental data.

Behaviour of thermodynamic properties

Adsorption and desorption isosteric heat values determined for Cape gooseberry samples are shown in Fig. 2 as a function of moisture content. The value of q_n decreased as moisture content increased, and as expected, desorption heat was higher than adsorption heat over the tested range of moisture content. This indicated that more energy was required for the moisture desorption process than for the moisture adsorption process (*34*). When moisture content of the dried Cape gooseberry increased from 0.25 to 2.50 g per g of dm, the heat of adsorption decreased from 6.65 to 0.02 kJ/mol; the heat

Table 3. Statistical results for the selected models of sorption isotherms of Cape gooseberry at 20, 40 and 60 °C

Model	Parameter	Adsorption			Desorption		
		Temperature/°C					
		20	40	60	20	40	60
GAB	R^2	0.9146	0.8562	0.7191	0.8871	0.8915	0.9374
	SSE	0.0077	0.0382	0.0056	0.0996	0.0002	0.0119
	χ^2	0.0102	0.0477	0.0069	0.1328	0.0002	0.0148
BET	R^2	0.7653	0.9536	0.8614	0.7690	0.9208	0.9052
	SSE	0.0003	0.0002	0.0002	0.0005	0.0002	0.0001
	χ^2	0.0005	0.0002	0.0002	0.0008	0.0002	0.0002
Henderson	R^2	0.9486	0.8731	0.9403	0.9894	0.9532	0.9642
	SSE	0.0096	0.0010	0.0002	0.1281	0.0003	0.0017
	χ^2	0.0119	0.0013	0.0002	0.1794	0.0005	0.0021
Caurie	R^2	0.9681	0.9139	0.8931	0.9678	0.9893	0.9649
	SSE	0.0200	0.0125	0.0168	0.0369	0.0667	0.0002
	χ^2	0.0250	0.0175	0.0205	0.0475	0.0857	0.0002
Smith	R^2	0.9097	0.8183	0.9363	0.9472	0.9773	0.9706
	SSE	0.0040	0.0008	0.0002	0.0007	0.0002	0.0001
	χ^2	0.0056	0.0010	0.0003	0.0011	0.0002	0.0002
Oswin	R^2	0.9726	0.9497	0.9521	0.9591	0.9744	0.9727
	SSE	0.0375	0.0086	0.0053	0.0322	0.0002	0.0792
	χ^2	0.0469	0.0120	0.0065	0.0451	0.0003	0.0990
Halsey	R^2	0.9483	0.9470	0.9660	0.9815	0.9864	0.9896
	SSE	0.0107	0.0082	0.0011	0.0077	0.0002	0.0058
	χ^2	0.0137	0.0102	0.0014	0.0103	0.0002	0.0072
Iglesias-Chirife	R^2	0.9898	0.9973	0.9856	0.9943	0.9734	0.9882
	SSE	0.0009	0.0004	0.0007	0.0030	0.0004	0.0002
	χ^2	0.0012	0.0005	0.0008	0.0045	0.0005	0.0003

SSE=sum of squared error
R^2=squared correlation coefficient
χ^2=reduced chi-square

of desorption of the fresh product decreased from 7.75 to 0.03 kJ/mol within the same range of moisture content. Similar values of q_n were reported by Talla *et al.* (*17*) for banana, mango, and pineapple.

The value of q_n was higher than that of the heat of vaporisation of pure water (*r*) for the entire moisture range, suggesting that the binding energy between water vapour molecules and the adsorption sites was higher than the energy of pure water molecules near the liquid phase (*32*). This behaviour indicated an interaction between water and the food matrix components, since with the decrease of moisture content in fresh product the spaces and active sites for water exit were reduced, implying a higher energy requirement for moving these water molecules (*38*). For some products, q_n can be negative, probably due to high sugar content, since with an increase in temperature, the equilibrium moisture increased due to solubility of food sugar and not to sorption behaviour (*27*). These changes are probably due to changes in molecular structure during sorption which affected the degree of activation of sorption sites. No
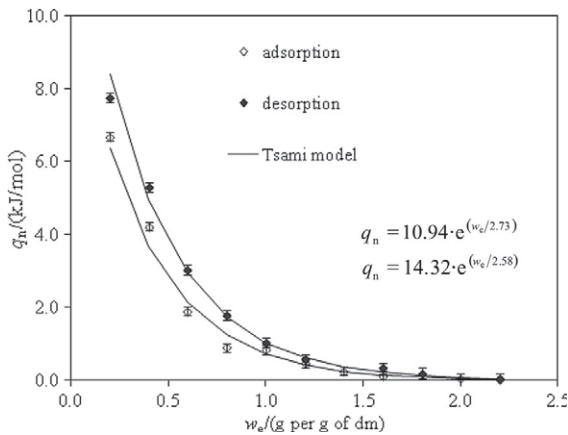
Fig. 2. Experimental and calculated net isosteric heat of sorption (q_n) of Cape gooseberry as a function of moisture content (w_e) per g of dry matter

Fig. 3. Changes in: a) entropy (S) and b) enthalpy (H) during adsorption and desorption of Cape gooseberry at various moisture contents (w_e) per g of dry matter

relationship existed between the degree of hysteresis and the variation in the isosteric heat of sorption (*18*). In addition, Fig. 2 also shows the modelling of isosteric heat (adsorption and desorption) by the Tsami equation (Eq. 14) (*20*). When applying this equation to model q_n in adsorption process, values of 109.89 kJ/mol and 0.1092 g per g of dm were obtained for q_o and w_o, respectively; and for modelling q_n in desorption process values of 229.51 kJ/mol and 0.1023 g per g of dm were obtained for q_o and w_o, respectively. Values of q_o between 40 and 115 kJ/mol and values of w_o between 0.08 and 0.21 g per g of dm were reported for other vegetables and fruits (*35*). For tropical pineapple values of 29.76 kJ/mol and 0.86 g per g of dm were reported for q_o and w_o respectively (*34*); in red bell pepper (var. Lamuyo) q_o value of 38.31 kJ/mol and w_o value of 0.19 g per g of dm were observed for adsorption, while q_o value of 75.51 kJ/mol and w_o value of 0.12 g per g of dm were reported for desorption (*16*).

These results showed a strong dependence of differential entropy and enthalpy on moisture content with a clear exponential trend (Fig. 3). This observation is similar to that reported by Goula *et al.* (*12*) and Al-Muhtaseb *et al.* (*18*), who studied the moisture sorption thermodynamic properties of spray-dried tomato pulp and starch powder, respectively. Adsorption entropy and enthalpy of Cape gooseberry decreased quickly with the increase in moisture content in the range of 0.2–1.2 g per g of dm from 0.24 to 0.015 kJ/(mol·K) and 78.7 to 5.0 kJ/mol, respectively (Fig. 3). Thereafter, it remained nearly constant until a moisture content of 2.5 g per g of dm was reached. The adsorption entropy and enthalpy values were greater than those for desorption at moisture content values between 0.2 and 0.6 g per g of dm. These values were then equalised as moisture content increased. Desorption entropy and enthalpy also decreased from 0.20 to 0.018 kJ/(mol·K) and from 75.8 to 5.8 kJ/mol respectively, as moisture content increased to a value of about 2.5 g per g of dm. In addition, adsorption entropy and enthalpy values were slightly higher than those for desorption at moisture content from 0.2 to 0.6 g per g of dm, thereafter these values were also equalised with an increase in moisture content.
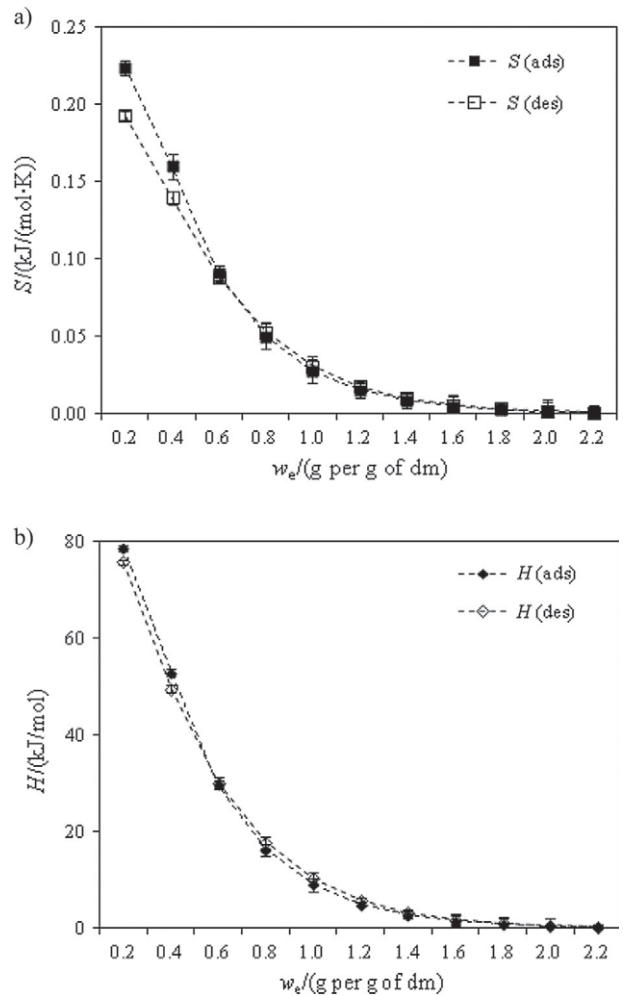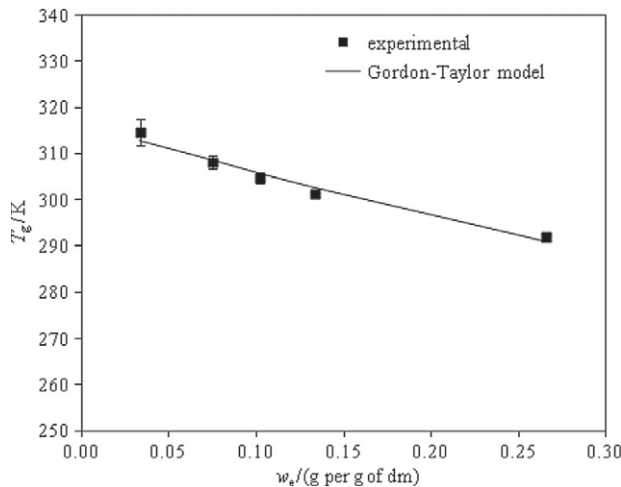
Behaviour of glass transition temperature

Figs. 4 and 5 show the glass transition temperature (T_g) values obtained for the Cape gooseberry samples as a function of moisture content and water activity, respectively. Both figures show that the water plasticisation effect caused a significant decrease in the glass transition temperature from 314.65 to 299.50 K with an increase in moisture content and water activity (*12*). Similar observation was reported by other researchers, who studied glass transitions and state diagrams for various fruits and vegetables (*39,40*). Telis and Sobral (*21*) determined the T_g of freeze-dried pineapple conditioned at various water activities and concluded that for a_w well below 0.90, the plasticising effect of water on the T_g was evident, with a great reduction of T_g caused by increasing moisture content. Roos and Karel (*41*) found dependence of T_g on water content, as water has a plasticising effect on the T_g of pectin, which leads to increased free volume and a weakening of the inter-chain interactions during storage. Sobral *et al.* (*42*) studied the phase diagram for freeze-dried persimmon and observed that in the hygroscopic domain (a_w<0.90), the plasticising effect was clear, whereas at water activities higher than 0.90,
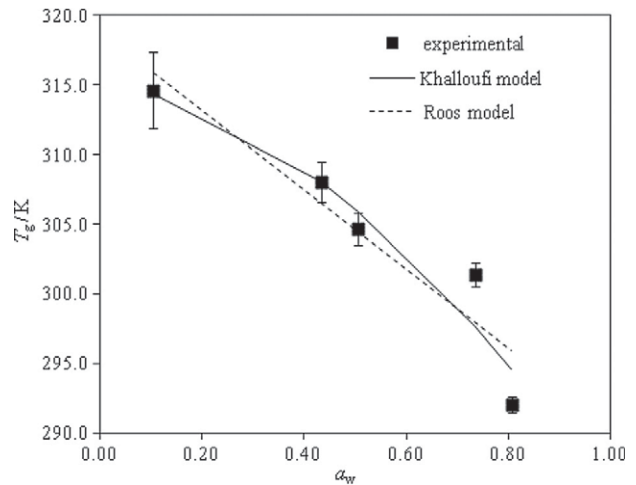
Fig. 4. Experimental and calculated values of glass transition temperature (T_g) of Cape gooseberry as a function of moisture content (w_e) per g of dry matter

Fig. 5. Experimental and calculated values of glass transition temperature (T_g) as a function of water activity (a_w) in Cape gooseberry

the glass transition curve exhibited a discontinuity, with a sudden increase of T_g that approached a constant value. This plasticising activity of water may be based on the weakening of hydrogen bonds and dipole-dipole intra- and inter-macromolecular interactions due to the shielding of these mainly attractive forces by water molecules. Fig. 4 shows the behaviour predicted by the Gordon--Taylor model. Large values for k in a binary mixture indicate large plasticising effect of the solids by water. The k=0.623 and T_{gs}=316.41 K parameters of the Gordon-Taylor model were estimated using non-linear optimisation while considering T_{gw}=138 K (R^2=0.97). The calculated T_{gs} and k values were similar to those reported for fruits, vegetables and sugar solutions (*24,37,39*). Telis and Sobral (*21*) found for freeze-dried pineapple T_{gs} and k values of 330.9 K and 0.21 respectively. Goula *et al.* (*12*) presented T_{gs} and k values of 603.9 K and 5.72, respectively, for spray-dried tomato pulp. Wang *et al.* (*40*) found T_{gs} and k values of 296.4 K and 9.35, respectively, for freeze-dried Chinese gooseberry. The differences in the values of the Gordon-Taylor parameters may be attributed to differences in product composition, drying preservation method and pretreatment types. In addition, Fig. 4 shows the critical water content obtained at a specific temperature, when glass transition occurred. If the product was commercialised at 25 °C, the critical value of water content at which the product 'glass' would be transformed to a liquid-like 'rubber' is 13 % on a dry basis. Above this value, Cape gooseberry would become sticky and the crystallisation of amorphous compounds could take place. Fig. 5 shows the data calculated by the Roos model (Eq. 21; R^2=0.89) and the model by Khalloufi *et al.* (*24*) (Eq. 22; R^2=0.92). These equations allow for a rapid and reliable method for calculating the T_g of Cape gooseberry stored under specific temperature and relative humidity conditions:

$$T_g=-28.44a_w+318.85 \qquad /21/$$

$$T_g = \frac{2.56 \cdot 10^{-8} a_w^2 + 2.34 \cdot 10^{-8} a_w + 315.2}{8.86 \cdot 10^{-2} a_w^2 + 1.54 \cdot 10^{-2} a_w + 1} \qquad /22/$$

Moisture sorption and glass transition

Both water activity and glass transition have proved to be useful to evaluate the storage stability of a food product. The a_w value would indicate the highest product stability at its monolayer moisture content, *i.e.* a water activity value of about 0.1–0.3, whereas according to T_g concept the formulations would be stable at or below the corresponding glass transition temperature. According to Roos (*43*) certain physicochemical and structural processes are better correlated to the glass transition temperature through plasticisation by water or temperature. These include stickiness, crispness, collapse, amorphous-to-crystalline transformations and the rates of non--enzymatic browning, which are not related to a monolayer value. The prevailing mechanism of these deteriorative processes is the molecular mobility that relates directly to T_g.

A glass transition in Cape gooseberry can be induced by either increasing temperature until T_g is exceeded or by introducing an increasing amount of water that acts as a plasticiser. Addition of water would lower viscosity, increase molecular mobility and free volume (*10*). As the amount of water is increased, the material would experience a change from the glassy to the rubbery state and would reach a state where it would no longer support its own mass and would collapse (*44*). If moisture were to continue to increase above the glass transition, molecular mobility would continue to rise causing an increase in the rate of time-dependent changes related to stability, such as stickiness, caking, collapse and crystallisation (*43*).

The influence of moisture on T_g of the Cape gooseberry samples was examined by performing thermal analysis on samples that had been equilibrated to different water activities, and hence different moisture contents. Multiple studies have shown a good correlation between water activity and T_g (*10*). This correlation is fairly linear over a water activity range between 0.1 and 0.7 (Fig. 5) as reported by various authors (*12,40,44*). Since T_g values will change as water activity or moisture content changes, all T_g values should specify the water

activity or moisture content at which they were measured.

Low molecular mass amorphous materials such as amorphous simple sugars have very low T_g values and are therefore susceptible to transitioning from a metastable glassy state to a less stable rubbery state under normal storage conditions. As the amount of water increases with increased water activity, the T_g decreases until at some water activity it is equal to room, experimental, or storage temperature. The water activity value that decreases the T_g to room temperature has been identified as the critical water activity, a_c (*45–47*). Like T_g, a_c is unique to each material type and has been shown to increase with an increase in the molecular mass of the amorphous material (*10*). For Cape gooseberry samples a_c is around 0.8 at 22 °C, but as temperature increased, a_c decreased, just as T_g decreased with an increase in relative humidity or water activity (Fig. 5). Since both temperature and moisture influence the glass transition, a T_g or an a_c should be reported with the corresponding water activity or temperature, respectively. Without these corresponding values, T_g and a_c have limited usefulness in practical application. The interdependency of T_g and a_c also suggests that both temperature and humidity abuse can cause an amorphous food to experience a glass transition and in turn decrease its stability.

For dried Cape gooseberry stored in bulk and exposed to ambient relative humidity, any rise in ambient humidity above a_c will result in a glass transition and the product will become susceptible to stickiness, caking, collapse and crystallization (*43*). Water activity monitoring can therefore be an effective tool to control the loss of stability that can occur if the product experiences a glass transition into the rubbery state. Conversely, if the dried Cape gooseberry is stored in good moisture barriers to prevent increases in water activity, but is exposed to temperatures higher than the T_g for the product at its natural water activity, it will experience a glass transition and again lose quality.

Conclusions

The moisture sorption isotherms of Cape gooseberry samples followed a sigmoid isotherm curve typical of the type I classification shape. Temperature affected the moisture sorption behaviour where equilibrium moisture content decreased with increasing temperature, at a constant water activity. The Iglesias-Chirife and Smith models were found to represent best the experimental data within the water activity range at the three temperatures studied. Tsami model was found to adequately describe the dependence of isosteric heat of sorption on the equilibrium moisture content. Water acts as a plasticiser in Cape gooseberry samples decreasing its T_g, while the Gordon-Taylor, Khalloufi and Roos models represent adequately the glass transition curve. T_g together with critical water activity are useful parameters in defining storage conditions.

Acknowledgements

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