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Modelling Thermodynamic Properties of Banana Waste by Analytical Derivation of Desorption Isotherms

Harvey A. Villa-Vélez, Henry A. Váquiro, José Bon, and Javier Telis-Romero

Abstract

Banana is an agricultural product of great economic importance for various developing countries. The relationship between moisture content and water activity provides useful information for the processing and storage of banana waste. The water activity and moisture content of three banana (*Mussa spp.* Haploid AAB cv. Nanica) waste items were analyzed to determine the desorption isotherms at six different temperatures (20, 30, 40, 50, 60 and 70°C). The desorption isotherms of the peel, pedicel and pulp of overripe bananas were determined in wide ranges of moisture content (0.001–6.360 kg kg⁻¹ d.b.) and water activity (0.02–0.907). The theoretical GAB model was used for modelling the desorption isotherms. An analytical solution of the Clausius-Clapeyron equation was proposed to compute the isosteric heat of sorption, the differential entropy and Gibbs' free energy by way of the GAB model when the effect of temperature on the hygroscopic equilibrium was considered.

KEYWORDS: sorption isotherms, GAB model, thermodynamic properties, banana waste, isosteric heat of sorption, water activity

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1. Introduction

Banana is one of the most extensively consumed fruits in the world and represents about 40% of the world trade in fruits. Brazil is the third most important banana producing country with a total production of up to 7 Mt, and the eighteenth in terms of exportation with a total of 185,721 t (FAO, 2007). Of all the bananas harvested about one-fifth are wasted and those rejected bananas are often improperly disposed of. It is estimated that close to 220 t of waste are generated per hectare of harvested banana, which are composed mainly of lignocellulosic material (Guyle'Ne et al., 2009; Zhang et al., 2005). Such waste contains from 8% to 18% of total solids and 86% to 92% of volatile solids, approximately. The organic fraction includes around 75% of biodegradable material (sugar and hemicellulose), 9% of cellulose and 5% of lignin, which are interesting sources of bioactive compounds. The rachis, pseudostem, leaf sheath and peel are the parts of the banana plant containing the largest amount of fibrous material. Due to their potential use as reinforcing components in high-performance composite materials, these cellulose-rich sources are currently being tested as heavy metal-adsorptive material in wastewater treatment, and as feedstock for bioethanol production (Bouallagui et al., 2005; Velásquez-Arredondo et al., 2010).

Drying and storage processes need to be developed for these wastes in order to achieve important advantages such as easy transportation, reduced microbial load, nutrient concentration and availability for processing (Prachayawarakorn et al., 2008). In this regard, an important aspect at the industrial level is the knowledge of the final moisture content and the energy required for drying, which are related to the hygroscopic equilibrium of the biological materials. A study of this equilibrium during the sorption isotherms allows for an understanding of the relationship between the equilibrium moisture content and the water activity within the foods, as well as the influence of their material structure and composition (Mulet et al., 2002).

A great number of mathematical models including two or more parameters have been used to represent the sorption isotherms. These models are classified as theoretical, semi-empirical or empirical (Barbosa-Cánovas et al., 2007). Those based on the kinetics of the monolayer, multilayer and condensed layer are grouped into theoretical models, where the parameters are functions of the physical properties of the material (Basu et al., 2006).

One of the models most widely used to describe the isotherms of foodstuffs and biological materials has been the Guggenheim, Anderson and de Boer (GAB) model (Eq. 1). This model often provides an adequate representation of the experimental data in a water activity range (0.10 ± 0.90) of practical interest in foods (Timmermann et al., 2001). The GAB equation has been recommended by the European Project Group COST90 (European Cooperation in Scientific and

Technical Research) to determine the physical properties of foods, and is known as the fundamental equation to characterize the water sorption of food materials (Cassini et al., 2006; Telis et al., 2000).

$$X_e = X_m \frac{CKa_w}{(1-Ka_w)[1+(C-1)Ka_w]} \quad (1)$$

In Eq. 1 a_w is the water activity, X_e is the equilibrium moisture content (kg kg^{-1} d.b.), X_m is the moisture content of the monolayer (kg kg^{-1} d.b.) and C and K are GAB model parameters. The GAB model parameters C and K can be written as temperature-dependent functions using Arrhenius type relationships:

$$C = C_0 \exp\left(\frac{H_m - H_n}{RT}\right) \quad (2)$$

$$K = K_0 \exp\left(\frac{\lambda - H_n}{RT}\right) \quad (3)$$

where C_0 and K_0 are GAB model parameters, H_m and H_n are the water sorption heats of the monolayer and multilayer (kJ mol^{-1}), respectively, λ is the vaporization energy of pure water (kJ mol^{-1}), T is the absolute temperature (K), and R is the ideal gas constant ($8.314 \text{ kJ K}^{-1} \text{ kmol}^{-1}$).

The thermodynamic properties of water and the moisture sorption isotherms are useful tools to determine water/material interactions and the water structure on the surface and inside of foods, and to provide useful information for assessing food processing operations such as drying, mixing and storage (Pérez-Alonso et al., 2006). Knowledge of the sorption isotherms at different temperatures enables one to evaluate the heat of sorption, which determines the interaction between an adsorbent and an adsorbate. Typically, determining this property means analysing the experimental data of the sorption isotherms using the Clausius-Clapeyron equation (Eq. 4) at constant moisture contents (McLaughlin and Magee, 1998; Yan et al., 2008b):

$$\frac{\partial(\ln a_w)}{\partial(1/T)} = -\frac{q_s}{R} \quad (4)$$

where q_s is the net heat of sorption. The isosteric heat of sorption (Q_{st}) (Eq. 5) is the sum of the net heat of sorption and the vaporization energy of pure water (λ) (Barbosa-Cánovas et al., 2007).

$$Q_{st} = q_s + \lambda \quad (5)$$

In general, the isosteric heat of sorption is greater than the latent heat of vaporization of pure water at a particular temperature, and can be considered as indicative of the intermolecular attraction forces between the sorptive sites and water.

Entropy changes may also be associated with the binding or repulsive forces in the system. Gibbs free energy (ΔG) may be indicative of the affinity of sorbents for water, and provides a criterion to determine whether water sorption occurs as a spontaneous ($\Delta G < 0$) or non-spontaneous ($\Delta G > 0$) process. By means of the Gibbs-Helmholtz equation (Eq. 6), the changes in differential molar entropy can be calculated (Simal et al., 2007):

$$\Delta S = \frac{q_s - \Delta G}{T} \quad (6)$$

where ΔS is the differential entropy ($\text{kJ mol}^{-1} \text{K}^{-1}$) and ΔG is Gibbs free energy (kJ mol^{-1}). ΔG is derived from the following equation (Basu et al., 2006):

$$\Delta G = RT \ln a_w \quad (7)$$

In thermodynamics, Gibbs free energy is known as a thermodynamic potential that measures the useful or process-initiating work obtainable from an isothermal, isobaric thermodynamic system. As in mechanics, where potential energy is defined as the capacity to do work, different potentials have different meanings. Free energy changes resulting from water sorption are usually accompanied by changes in both enthalpy and entropy (García et al., 2008). Substituting Eq. 7 in Eq. 6 and rearranging the terms, the following equation is obtained:

$$\ln a_w = \frac{q_s}{RT} - \frac{\Delta S}{R} \quad (8)$$

Knowledge of the effect of temperature on the sorption phenomena provides helpful information with respect to energy changes in the system. Temperature dependence on water activity can be estimated by using thermodynamic principles and sorption equations as functions of temperature (Basu et al., 2006). During adsorption, differential entropy will be negative because the adsorbate-sorbate system becomes ordered upon adsorption and loses degrees of freedom. If ΔG is less than zero, q_s will have to be negative (Eq. 6) and thus adsorption is exothermic. Similarly, desorption can be shown to be endothermic. Likewise, an

increase in temperature will cause a corresponding decrease in ΔS , because ΔG depends slightly on the temperature, which causes a decrease in the number of molecules adsorbed. Therefore, in general, adsorption decreases when the temperature increases. Although greater adsorption levels occur at lower temperatures, the entropy differences are usually small. At times, however, larger entropy differences are observed. Although there is not a particular trend that represents these entropy differences, the temperature can affect several factors at the same time. For instance, an increase in temperature may increase the rates of adsorption, hydrolysis and recrystallization reactions (Barbosa-Cánovas et al., 2007; Rizvi, 2005).

At present, data on the sorption isotherms and thermodynamic properties of the water in agricultural waste is limited. The objective of this work was to provide experimental sorption isotherm data for the peel, pedicel and pulp of overripe bananas at various temperatures in order to model this behaviour, and hence estimate the isosteric heat of sorption, the differential entropy and Gibbs free energy for each waste item.

2. Material and Methods

2.1. Raw material

Samples of the peel, pedicel and pulp of overripe bananas (*Musa acuminata AAA* cv. Dwarf Cavendish) were used in this study. Overripe bananas in the condition of waste were obtained from a local market in São José do Rio Preto (São Paulo, Brazil). The raw material was stored at 15 °C for twenty-four hours prior to analysis.

2.2. Sample preparation

Once the overripe bananas were cleaned and disinfected, the pedicel was cut from the fruit and the pulp separated from the peel. Each waste item (peel, pedicel and pulp) was reduced to particle sizes between 0.1 and 0.5 ± 0.05 mm using a food grinder (model RI17625/71, Philips, Japan) until 200 g of each sample was obtained.

2.3. Determination of the desorption isotherms

The equilibrium moisture contents of the peel, pedicel and pulp were determined by triplicate using the static gravimetric method (Jowitt et al., 1983) at temperatures of 20, 30, 40, 50, 60 and 70 °C. The experimental setup consisted of nine hermetic glass jars containing different, saturated salt solutions (NaOH, LiCl, $KC_2H_3O_2$, $MgCl_2$, K_2CO_3 , $Mg(NO_3)_2$, $NaNO_2$, NaCl, KCl, $BaCl_2$). These

solutions gave corresponding values of relative humidity (RH) from 2 to 90%. Each jar was filled to a depth of 1.5 cm with the appropriate salt solution. For each measurement, three replicates of about 1 g of sample were placed in small plastic containers, which in turn were placed on a support in each jar in order to avoid contact with the salt solution. The jars were subsequently placed in a temperature-controlled chamber (BOD, Model TE-391, TECNAL, Brazil) under different temperature and relative humidity conditions, according to the salt used in the jar. The sample weights were controlled until the moisture content on a dry weight basis did not exceed 0.1% (time elapsed-from 4 to 5 weeks), at which point equilibrium was assumed, thus assuring that the water activity of each sample corresponded to relative humidity. For each waste, the initial moisture content was determined according to the AOAC method 926.12 (AOAC, 1997) to determine the equilibrium moisture content from the registered weight up to equilibrium. The values obtained for the equilibrium moisture contents, water activities, and temperatures were used to construct the desorption isotherms for the banana peel, pedicel and pulp.

2.4. *Modelling the sorption isotherms*

The GAB model was used to model the water sorption behaviour of the overripe banana waste. Modelling was carried out by establishing the parameters X_m , H_m , H_n , C_0 and K_0 of Eqs. 1–3 by fitting the GAB model to experimental data of the sorption isotherm. The fitting procedure was based on the so-called direct method. This method involved substituting Eqs. 2 and 3 in the GAB model (Eq. 1), and the parameters were identified by using the experimental results obtained for the equilibrium moisture contents at the different water activities and temperatures simultaneously (Mulet et al., 1999; Simal et al., 2007).

The fit was constricted by limiting the effects of both temperature and moisture content when considered simultaneously; thus the monolayer moisture content should be constant in the temperature range studied for each waste item, in order to accomplish thermodynamic equilibrium.

2.5. *Deriving the isosteric heat of sorption from the GAB model*

To assess the isosteric heat, the net isosteric heat of sorption was computed using the Clausius-Clapeyron equation (Eq. 4), and the ASAE Standards (ASAE, 1999) were used to estimate the heat of vaporization of pure water (λ) in relation to the temperature:

$$q_s = -R \frac{\partial(\ln a_w)}{\partial(1/T)} = \frac{RT^2}{a_w} \frac{\partial a_w}{\partial T} \quad (9)$$

To compute the Clausius-Clapeyron equation, the GAB model was used to determine the analytical partial derivative of the water activity with respect to the temperature. The errors associated with experimental assays, jointly with natural variability, constitute the main disadvantage of this technique as compared to those based on deriving isosteric heat equations from GAB model calorimetric methods (Mulet et al., 1999), which is a good alternative if proper instrumentation is available.

For the water activity calculus, the GAB equation (Eq. 1) can be rearranged as follows:

$$(C-1)K^2a_w^2 + [2 - C(1 - X_m/X_e)]Ka_w - 1 = 0 \quad (10)$$

Considering the following coefficients, α and β , Eq. 10 transforms to a quadratic form (Eq. 13):

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

$$\beta = [2 - C(1 - X_m/X_e)]K \quad (12)$$

$$\alpha a_w^2 + \beta a_w - 1 = 0 \quad (13)$$

The correct solution for Eq. 13 was obtained using the positive root of the quadratic formula:

$$a_w = \frac{-\beta + (\beta^2 + 4\alpha)^{1/2}}{2\alpha} \quad (14)$$

By deriving the previous expression with respect to time when X_m is constant, and by using the relationships $(2\alpha a_w + \beta) = (\beta^2 + 4\alpha)^{1/2}$ and $\alpha a_w^2 = 1 - \beta a_w$, obtained from Eqs. 14 and 13, the analytical partial derivative of water activity was obtained:

$$\frac{\partial a_w}{\partial T} = \frac{(\beta a_w - 1) \frac{d\alpha}{dT} - \alpha a_w \frac{d\beta}{dT}}{\alpha(2\alpha a_w + \beta)} \quad (15)$$

where

$$\frac{d\alpha}{dT} = 2K(C-1) \frac{dK}{dT} + K^2 \frac{dC}{dT} \quad (16)$$

$$\frac{d\beta}{dT} = 2 \frac{dK}{dT} - \left(C \frac{dK}{dT} + K \frac{dC}{dT} \right) \left(1 - \frac{X_m}{X_e} \right) \quad (17)$$

$$\frac{dC}{dT} = -C_0 \frac{H_m - H_n}{RT^2} \exp\left(\frac{H_m - H_n}{RT}\right) \quad (18)$$

$$\frac{dK}{dT} = -K_0 \frac{(\lambda - H_n) - T \frac{d\lambda}{dT}}{RT^2} \exp\left(\frac{\lambda - H_n}{RT}\right) \quad (19)$$

2.6. Determination of the thermodynamic properties

Net isosteric heat of sorption of water (q_s , Eq. 9) was estimated for the peel, pedicel and pulp at moisture contents between 0.001 and 0.8 kg kg⁻¹ (d.b.) and at temperatures of 20 and 70 °C. The value for q_s was calculated for the minimum and maximum temperatures used in this study, with the aim of finding a significant difference in the results for each waste item.

The differential entropy (ΔS) was obtained directly from Eq. 8, unlike the conventional procedure where ΔS is obtained by plotting $\ln a_w$ versus $1/T$ and calculating the slope of the line (q_s/R) and the y -intercept ($-\Delta S/R$) (Mulet et al., 1999; Sánchez et al., 1997). The direct procedure avoids the uncertainty associated with linearization. The water activities correspond to those used for calculating q_s at the temperatures of 20 and 70 °C.

Gibbs free energy (ΔG) was calculated from Eq. 7 at the temperatures of 20 and 70 °C for the three waste items. The water activities corresponded to those used to calculate q_s at the same temperatures.

2.7. Estimation of the parameters and statistical analysis

The GAB model parameters (X_m , H_m , H_n , C_0 and K_0 ; Eqs. 1–3) were estimated by fitting the equations to the experimental data using the *nlinfit* function of the Statistic Toolbox of Matlab® 7.1 (The MathWorks Inc., Natick, MA, USA) and considering the robust fitting option. This function uses the Gauss-Newton algorithm with Levenberg-Marquardt modifications that iteratively reweighs the response values and re-computes a least-square fit of a non-linear model. The 95% confidence intervals of the estimated GAB parameters were determined by using the *nlparci* function of the same Matlab Toolbox.

The coefficient of determination (R^2) (Eq. 20) and the root mean square error (*RMSE*) (Eq. 21) were used to assess the model accuracy. The statistical parameter R^2 defines how successfully the model explains the variation in the

data, while *RMSE* is a measure of the standard error in the estimation (Sheskin, 2004).

$$R^2 = \frac{\sum_{k=1}^N (y_k^* - \bar{y})^2}{\sum_{k=1}^N (y_k - \bar{y})^2} \quad (20)$$

$$RMSE = \left[\frac{1}{N} \sum_{k=1}^N (y_k - y_k^*)^2 \right]^{1/2} \quad (21)$$

In Eqs. 20 and 21, y represents the experimental values; y^* represents the estimated values; \bar{y} is the average of the experimental values, and N is the number of experimental values.

3. Results and Discussion

3.1. Experimental desorption isotherm data

Tables 1, 2 and 3 show the experimental data for the peel, pedicel and pulp, respectively, with the corresponding standard deviations for three replicates. The equilibrium moisture content ranged from 6.360 to 0.001 kg kg⁻¹ (d.b.) in the whole range of water activities considered. The desorption isotherm data for each waste item (Fig. 1) indicated curves that were characteristic of products with high sugar and water contents, at the high relative humidity levels (curves type III) (Barbosa-Cánovas et al., 2007; Brunauer et al., 1940).

For the peel and pedicel of the overripe bananas (Tables 1 and 2, Fig. 1) at a temperature of 20 °C and a water activity of 0.907, equilibrium moisture contents of 6.360 and 5.910 kg kg⁻¹ (d.b.) were obtained, respectively. These values decreased as the temperature increased, whilst at a temperature of 70 °C and a water activity of 0.870 equilibrium moisture contents of 0.750 and 0.689 (d.b.) were reached for the peel and pedicel, respectively. These waste items are mainly composed of cellulose and hemicellulose, and at low temperatures, when the saturation pressure is smaller in the system, they may be able to absorb water (Gomez-Carracedo et al., 2010).

In order to explain the strong relationship between temperature and water activity, some papers have indicated that the decrease in moisture content is due to an increase in the excited state of the water molecules at high temperatures, increasing the distances between the molecules and reducing their attractive forces. Other studies have suggested that the increase in temperature causes incorporation of water, which reduces the number of active sites and promotes physical or chemical changes in the material of study (Al-Muhtaseb et al., 2002; Samapundo et al., 2007).

Table 1. Experimental equilibrium moisture contents for the banana peel* at temperatures ranging from 20 to 70 °C.

<i>T</i>	<i>a_w</i>	<i>X_e</i>	<i>T</i>	<i>a_w</i>	<i>X_e</i>	<i>T</i>	<i>a_w</i>	<i>X_e</i>
20	0.070	0.006 ±0.000	30	0.069	0.006 ±0.000	40	0.066	0.005 ±0.000
	0.113	0.010 ±0.000		0.112	0.010 ±0.000		0.111	0.009 ±0.000
	0.246	0.025 ±0.001		0.223	0.025 ±0.001		0.206	0.019 ±0.000
	0.331	0.037 ±0.001		0.324	0.038 ±0.001		0.319	0.035 ±0.001
	0.446	0.062 ±0.001		0.439	0.064 ±0.001		0.432	0.057 ±0.000
	0.547	0.096 ±0.003		0.526	0.090 ±0.003		0.506	0.076 ±0.001
	0.655	0.160 ±0.002		0.635	0.171 ±0.002		0.615	0.132 ±0.001
	0.754	0.305 ±0.003		0.756	0.326 ±0.004		0.753	0.295 ±0.001
	0.853	0.904 ±0.019		0.835	0.692 ±0.019		0.820	0.532 ±0.007
0.907	6.360 ±0.107	0.900	4.774 ±0.058	0.893	2.604 ±0.054			
<i>T</i>	<i>a_w</i>	<i>X_e</i>	<i>T</i>	<i>a_w</i>	<i>X_e</i>	<i>T</i>	<i>a_w</i>	<i>X_e</i>
50	0.059	0.004 ±0.000	60	0.045	0.002 ±0.000	70	0.020	0.001 ±0.000
	0.110	0.007 ±0.000		0.110	0.006 ±0.000		0.110	0.005 ±0.000
	0.189	0.013 ±0.001		0.175	0.011 ±0.000		0.162	0.009 ±0.000
	0.314	0.024 ±0.000		0.307	0.023 ±0.000		0.294	0.018 ±0.001
	0.432	0.045 ±0.001		0.432	0.040 ±0.000		0.432	0.033 ±0.000
	0.489	0.057 ±0.003		0.473	0.048 ±0.001		0.458	0.036 ±0.001
	0.599	0.095 ±0.001		0.590	0.080 ±0.002		0.587	0.070 ±0.000
	0.746	0.217 ±0.004		0.740	0.190 ±0.002		0.739	0.153 ±0.003
	0.809	0.375 ±0.013		0.800	0.317 ±0.009		0.795	0.237 ±0.006
0.884	1.428 ±0.023	0.876	0.950 ±0.009	0.870	0.750 ±0.026			

Table 2. Experimental equilibrium moisture contents for the banana pedicel* at temperatures ranging from 20 to 70 °C.

<i>T</i>	<i>a_w</i>	<i>X_e</i>	<i>T</i>	<i>a_w</i>	<i>X_e</i>	<i>T</i>	<i>a_w</i>	<i>X_e</i>
20	0.070	0.006 ±0.000	30	0.069	0.005 ±0.000	40	0.066	0.005 ±0.000
	0.113	0.009 ±0.000		0.112	0.009 ±0.000		0.111	0.008 ±0.000
	0.246	0.023 ±0.001		0.223	0.025 ±0.001		0.206	0.018 ±0.000
	0.331	0.034 ±0.000		0.324	0.034 ±0.000		0.319	0.033 ±0.000
	0.446	0.056 ±0.000		0.439	0.057 ±0.001		0.432	0.053 ±0.000
	0.547	0.087 ±0.002		0.526	0.076 ±0.003		0.506	0.068 ±0.001
	0.655	0.144 ±0.002		0.635	0.168 ±0.002		0.615	0.124 ±0.001
	0.754	0.283 ±0.002		0.756	0.288 ±0.004		0.753	0.274 ±0.002
	0.853	0.857 ±0.009		0.835	0.592 ±0.016		0.820	0.480 ±0.004
0.907	5.910 ±0.028	0.900	4.700 ±0.057	0.893	2.420 ±0.009			
<i>T</i>	<i>a_w</i>	<i>X_e</i>	<i>T</i>	<i>a_w</i>	<i>X_e</i>	<i>T</i>	<i>a_w</i>	<i>X_e</i>
50	0.059	0.004 ±0.000	60	0.045	0.002 ±0.000	70	0.020	0.010 ±0.000
	0.110	0.007 ±0.000		0.110	0.005 ±0.000		0.110	0.005 ±0.000
	0.189	0.012 ±0.001		0.175	0.009 ±0.001		0.162	0.008 ±0.000
	0.314	0.023 ±0.000		0.307	0.023 ±0.001		0.294	0.016 ±0.000
	0.432	0.040 ±0.001		0.432	0.035 ±0.001		0.432	0.030 ±0.000
	0.489	0.053 ±0.002		0.473	0.042 ±0.003		0.458	0.032 ±0.000
	0.599	0.088 ±0.001		0.590	0.068 ±0.001		0.587	0.062 ±0.000
	0.746	0.197 ±0.004		0.740	0.187 ±0.007		0.739	0.141 ±0.001
	0.809	0.348 ±0.012		0.800	0.280 ±0.018		0.795	0.222 ±0.002
0.884	1.282 ±0.021	0.876	0.839 ±0.029	0.870	0.689 ±0.002			

*Mean and standard deviation for three replicates. *T*: temperature (°C); *X_e*: experimental equilibrium moisture content (kg kg⁻¹ d.b.); *a_w*: water activity (dimensionless).

Table 3. Experimental equilibrium moisture contents for the banana pulp* at temperatures ranging from 20 to 70 °C.

<i>T</i>	<i>a_w</i>	<i>X_e</i>	<i>T</i>	<i>a_w</i>	<i>X_e</i>	<i>T</i>	<i>a_w</i>	<i>X_e</i>
20	0.070	0.015 ±0.000	30	0.069	0.011 ±0.000	40	0.066	0.009 ±0.000
	0.113	0.025 ±0.001		0.112	0.018 ±0.001		0.111	0.015 ±0.000
	0.246	0.056 ±0.000		0.223	0.045 ±0.001		0.206	0.032 ±0.000
	0.331	0.079 ±0.001		0.324	0.063 ±0.001		0.319	0.056 ±0.000
	0.446	0.118 ±0.001		0.439	0.099 ±0.002		0.432	0.089 ±0.001
	0.547	0.164 ±0.001		0.526	0.129 ±0.005		0.506	0.114 ±0.001
	0.655	0.234 ±0.003		0.635	0.223 ±0.001		0.615	0.182 ±0.002
	0.754	0.354 ±0.003		0.756	0.327 ±0.006		0.753	0.325 ±0.002
	0.853	0.848 ±0.017		0.835	0.737 ±0.020		0.820	0.735 ±0.013
0.907	1.514 ±0.010	0.900	1.734 ±0.033	0.893	1.526 ±0.009			
<i>T</i>	<i>a_w</i>	<i>X_e</i>	<i>T</i>	<i>a_w</i>	<i>X_e</i>	<i>T</i>	<i>a_w</i>	<i>X_e</i>
50	0.059	0.007 ±0.000	60	0.045	0.004 ±0.000	70	0.02	0.001 ±0.016
	0.110	0.012 ±0.000		0.110	0.010 ±0.000		0.110	0.008 ±0.000
	0.189	0.022 ±0.001		0.175	0.017 ±0.001		0.162	0.014 ±0.000
	0.314	0.042 ±0.001		0.307	0.035 ±0.001		0.294	0.029 ±0.001
	0.432	0.078 ±0.002		0.432	0.068 ±0.002		0.432	0.056 ±0.001
	0.489	0.097 ±0.004		0.473	0.080 ±0.003		0.458	0.061 ±0.001
	0.599	0.154 ±0.001		0.590	0.134 ±0.002		0.587	0.126 ±0.002
	0.746	0.292 ±0.005		0.740	0.267 ±0.003		0.739	0.240 ±0.001
	0.809	0.688 ±0.019		0.800	0.637 ±0.016		0.795	0.558 ±0.008
0.884	1.341 ±0.027	0.876	1.161 ±0.023	0.870	1.080 ±0.036			

*Mean and standard deviation for three replicates. *T*: temperature (°C); *X_e*: experimental equilibrium moisture content (kg kg⁻¹ d.b.); *a_w*: water activity (dimensionless).

The data of the experimental desorption isotherm data for the pulp of the overripe bananas (Table 3, Fig. 1) did not present significant differences in the equilibrium moisture content with increased temperatures as in the case of the water activity. For this product, the equilibrium moisture content was between 0.001 and 1.734 kg kg⁻¹ (d.b.) at water activities between 0.002 and 0.900 in the temperature range between 20 and 70 °C. Yan et al., (2008b) published experimental data for banana pulp with equilibrium moisture content between 0.001 and 1.4 kg kg⁻¹ (d.b.), water activity between 0.060 and 0.870 and temperatures of 20, 30, and 40 °C. At temperatures of 50, 60 and 70 °C low equilibrium moisture contents were observed, and this can be explained by the increased solubility of the large amounts of crystallized sugar in the banana pulp.

The moisture content/temperature relationship has an important role in the chemical and microbiological reactions in order to prevent a rapid deterioration of products with high sugar and water contents (Telis et al., 2000; Yan et al., 2008a; Yan et al., 2008b).

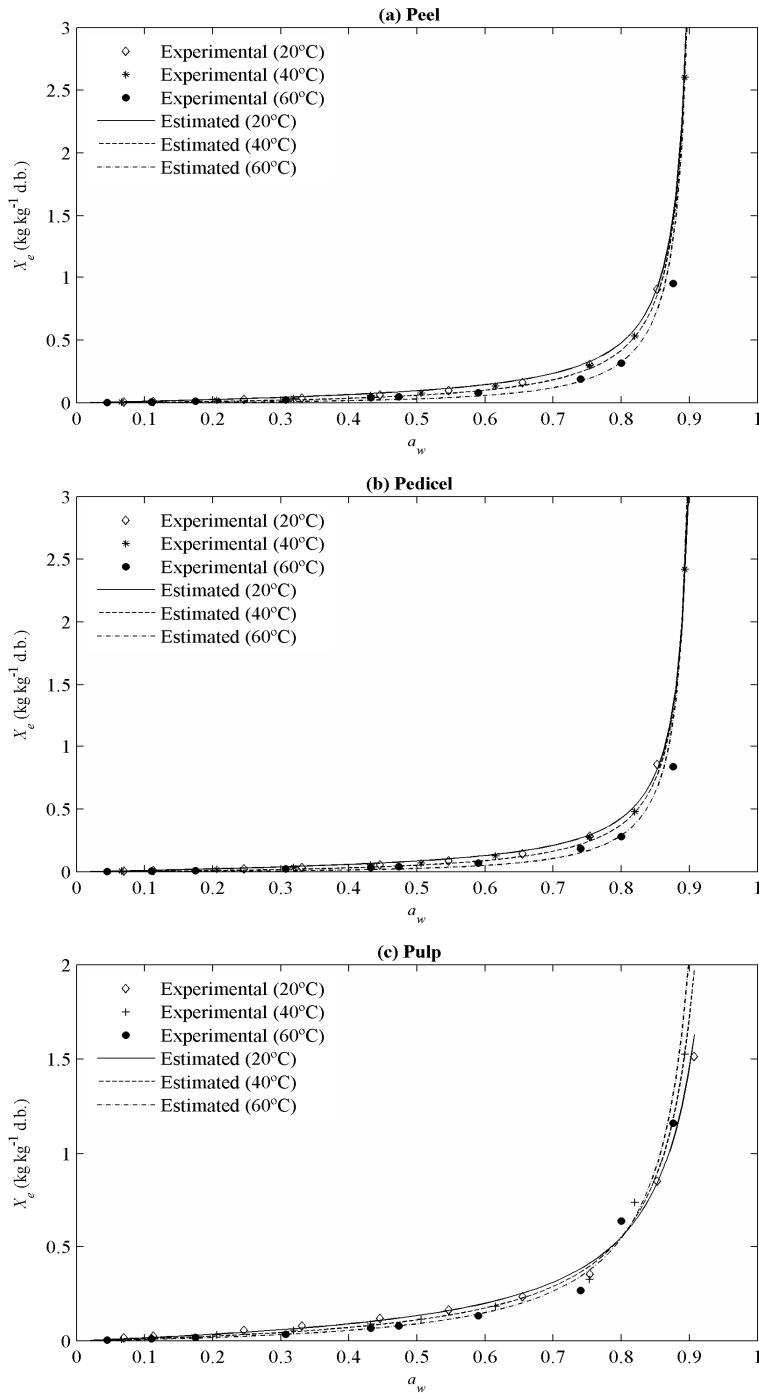


Figure 1. Experimental sorption isotherms for the peel (a), pedicel (b) and pulp (c) of overripe bananas at 20, 40 and 60 °C and the results estimated with the GAB model

3.2. Fitting the GAB model to the experimental desorption data

Table 4 shows the statistical validations and results for the parameters of the GAB model. The statistical results show coefficients of determination of 97.79%, 97.06% and 98.83% for the peel, pedicel and pulp, respectively, indicating a satisfactory agreement between the experimental and estimated values. The confidence intervals for the GAB model parameters at the 95% confidence level are shown in Table 5.

Table 4. Estimated GAB model parameters and statistical results.

Waste item	Parameters					R^2	RMSE
	X_m	C_0	K_0	H_m	H_n		
Peel	6.567×10^{-2}	1.326×10^{-7}	192.1	96.68	56.79	97.79	0.1571
Pedicel	5.904×10^{-2}	8.502×10^{-8}	195.1	97.82	56.83	97.06	0.1713
Pulp	1.138×10^{-1}	1.123×10^{-3}	221.4	74.42	57.28	98.83	0.0462

X_m : monolayer average equilibrium moisture content (kg kg^{-1} d.b.); C_0 and K_0 : GAB model parameters (dimensionless); H_m : monolayer sorption heat (kJ mol^{-1}); H_n : multilayer sorption heat (kJ mol^{-1}).

Table 5. Confidence intervals for the GAB model parameters.

Waste item	X_m	95% confidence intervals			
		C_0	K_0	H_m	H_n
Peel	3.857×10^{-2}	-2.746×10^{-6}	173.0	35.56	56.55
	9.277×10^{-2}	3.012×10^{-6}	211.3	157.80	57.03
Pedicel	2.915×10^{-2}	-2.134×10^{-6}	173.1	24.24	56.56
	8.893×10^{-3}	2.304×10^{-6}	217.2	171.41	57.10
Pulp	0.0857	-3.965×10^{-3}	209.4	61.70	57.14
	0.1418	6.210×10^{-3}	233.3	87.14	57.42

X_m : monolayer average equilibrium moisture content (kg kg^{-1} d.b.); C_0 and K_0 : GAB model parameters (dimensionless); H_m : monolayer sorption heat (kJ mol^{-1}); H_n : multilayer sorption heat (kJ mol^{-1}).

The comparisons between the experimental and estimated values for the isotherms at 20, 30, 40, 50, 60 and 70 °C for each waste item, using the GAB model are shown in Fig. 1. Table 6 shows the corresponding correlation coefficients and the root mean square errors.

The estimated values for X_m (constant between 20 and 70 °C) were 6.567×10^{-2} , 9.04×10^{-2} and 1.138×10^{-2} kg kg^{-1} (d.b.) for the peel, pedicel and pulp, respectively. Moreover, for the three waste items the calculated values for C gradually decreased as the temperature increased and the calculated values for K increased as the temperature increased. For all the waste items, the values for the constant K were below one, such results indicating that there was a difference in

free enthalpy between the sorbate molecules in the pure liquid and those in the second sorption stage in the layer above the monolayer (Basu et al., 2006).

Table 6. The coefficients of determination (R^2) and root mean square errors ($RMSE$) for the modelling of the sorption isotherms for the peel, pedicel and pulp of overripe bananas.

Waste item	T (°C)	R^2	$RMSE$
Peel	20	99.98	0.2440
	30	99.90	0.2833
	40	99.99	0.0125
	50	99.89	0.1105
	60	99.14	0.1129
	70	99.76	0.0176
	Pedicel	20	99.99
30		99.72	0.3983
40		99.98	0.0206
50		99.80	0.1102
60		98.72	0.1158
70		99.73	0.0182
Pulp		20	99.76
	30	99.41	0.0548
	40	99.42	0.0351
	50	98.94	0.0441
	60	98.27	0.0606
	70	98.99	0.0348

The estimated heat of sorption of the monolayer (H_m) were 96.68, 97.82 and 74.42 kJ mol⁻¹ for the peel, pedicel and pulp of the overripe bananas, respectively (using values of λ between 44.2 and 42.0 kJ mol⁻¹, values within the temperature range of 20 to 70 °C). These values were of the same order as those proposed by different authors: 97.0 kJ mol⁻¹ for pineapple (Simal et al., 2007); 50.6 kJ mol⁻¹ for morel (Mulet et al., 2002); and 43.0 kJ mol⁻¹ for lemon peel (García-Pérez et al., 2008). For the estimated heat of sorption of the multilayer (H_n), values of 56.79, 56.83, and 57.28 kJ mol⁻¹ were found for the peel, pedicel and pulp, respectively. These values were very close, which is consistent with the theory suggesting that the state of the sorbate molecules in the second and higher layers is equal, but different from that in the liquid-like state (Al-Muhtaseb et al., 2002).

3.3. *Isosteric heat of sorption*

The Clausius-Clapeyron equation was used to compute the isosteric heat of sorption for the peel, pedicel and pulp using the GAB model.

The isosteric heat of sorption found at temperatures of 20 and 70 °C are shown in Fig. 2. These curves showed values that were very close for all the waste items, in agreement with reports in the literature concerning about the closeness between the two methods for estimating isosteric heat of sorption (García-Pérez et al., 2008; Yan et al., 2008b).

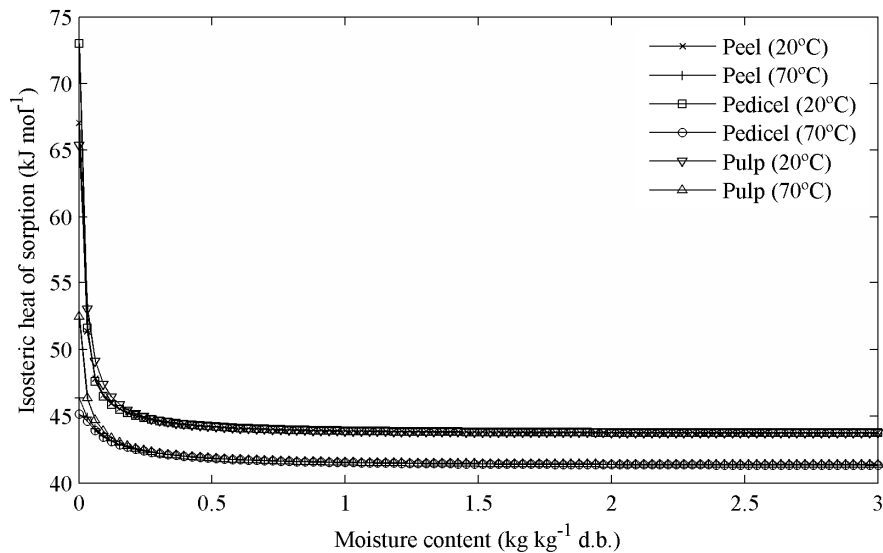


Figure 2. Isosteric heat of sorption for water desorption from the peel, pedicel and pulp of overripe bananas, at temperatures of 20 and 70 °C, as a function of the moisture content.

The isosteric heat values decreased as the moisture content increased, and were close to the water vaporization energy at moisture contents of over 0.5 kg kg⁻¹ (d.b). This can be explained quantitatively by considering that, at low moisture contents, sorption occurs at the most active available sites, giving rise to great interaction energy. The initial values for the heat may have resulted from the chemisorption on polar groups. The value of q_s was higher than zero, but tending to zero as the moisture content increased (Mulet et al., 1999; Telis et al., 2000).

3.4. Differential entropy

Fig. 3 shows the evolution of differential entropy with the moisture content at temperatures of 20 and 70 °C.

The differential entropy represents the algebraic sum of the integral entropy at a particular hydration level, plus the change of order or disorder after new water molecules are adsorbed by the system at the same hydration level. If the values for moisture content corresponding to the minimum integral entropy and minimum

differential entropy are different, the particular hydration level at the minimum differential entropy cannot be considered as the maximum stability point, because not all the available active sites have been occupied at that particular water content, and therefore after this point it is possible to obtain lower differential changes that provide a better ordering of the water molecules adsorbed on the food (Simal et al., 2007; Telis et al., 2000). In this case the water content at the minimum differential entropy was similar to the values obtained in the GAB monolayer, because the maximum entropy change was caused by the water sorption at the most active sites. The value obtained for the monolayer represented the saturation of the polar groups, corresponding to the water adsorbed at the most active sites.

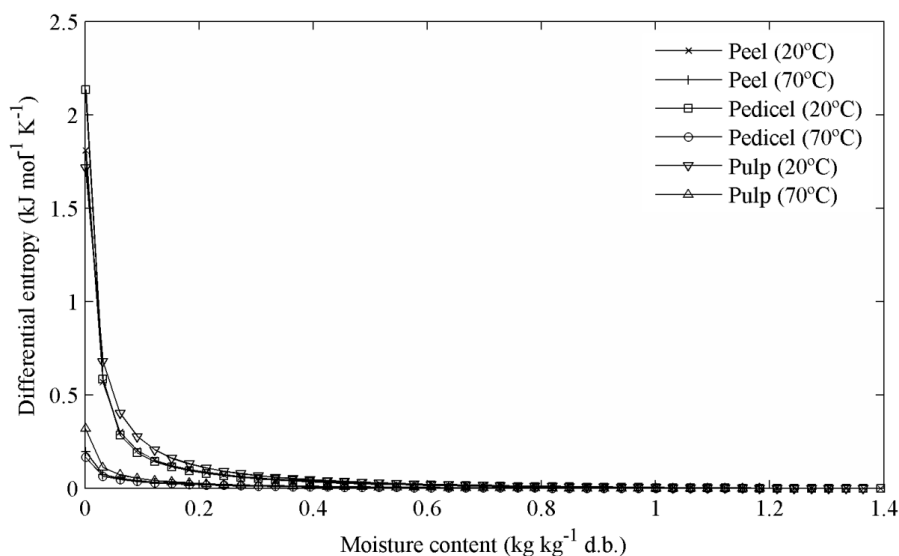


Figure 3. Differential entropy for water desorption from the peel, pedicel and pulp of overripe bananas, as a function of the moisture content.

3.5. Enthalpy-entropy compensation

Fig. 4 shows curves that are very close to each other for the peel, pedicel, and pulp at temperatures of 20 and 70 °C showing values that were very similar in the moisture content range studied, the values for ΔG all being less than zero for the three waste items. The ΔG results indicate that water sorption occurred in a spontaneous process. Moreover, the values showed that the reactions occurring in the microstructure of the product would remain stable throughout the temperature range of 20-70 °C. In general terms, Figs. 2 and 3 showed stronger intermolecular interactions or bonding (related to the enthalpy), which would lead to a greater reduction in the freedom of configuration and hence to a greater order of the

system (related to the entropy). This relationship might allow for the application of the enthalpy-entropy compensation theory to the three waste items, since the reaction rate should be similar for all the reactions occurring at the temperatures evaluated.

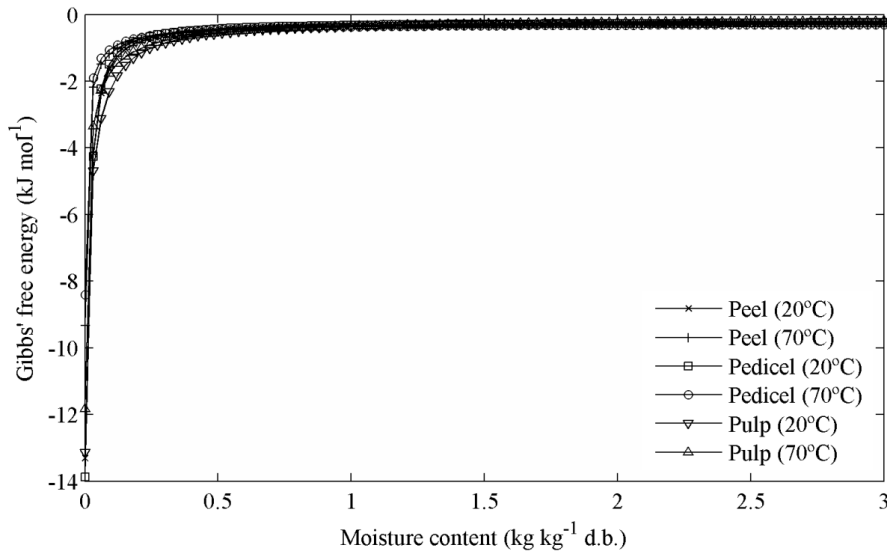


Figure 4. Gibbs free energy for water desorption from the peel, pedicel and pulp of overripe bananas, as a function of the moisture content.

The existence of the compensation theory implies that only one reaction mechanism is followed by all members of the reaction series and, therefore, a reliable evaluation of the isokinetic relationship aids elucidation of the reaction mechanisms (García et al., 2008).

4. Conclusions

Sorption isotherms for the peel, pedicel and pulp of overripe bananas were experimentally determined at 20, 30, 40, 50, 60 and 70 °C, in a wide range of water activity and moisture content values. The GAB model was used to adequately represent the desorption data of the three waste items, at the study temperatures. The GAB model can be used to determine the analytical partial derivative of the water activity with respect to the temperature in the computation of the Clausius-Clapeyron equation, in order to determine the net isosteric heat of sorption of the water. The application of the above methodology allows one to calculate the value for q_s directly, avoiding the linearization between a_w versus $1/T$ as proposed and used by most authors. Moreover, the values for ΔS and ΔG were also calculated directly in the moisture content range of the isotherm

desorption for each waste item. Finally the enthalpy-entropy compensation suggested a thermodynamic equilibrium, where, from an analysis of ΔG in the same moisture contents range, a spontaneous process for the three waste items studied was observed.

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