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Water sorption isotherms and glass transition temperature of spray dried tomato pulp

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Abstract

Adsorption isotherms of tomato pulp spray dried in dehumidified air were determined at six temperatures between 20 and 70 °C using a gravimetric technique. The data obtained were fitted to several models including two-parameter (BET, Halsey, Smith and Oswin), three-parameter (GAB), and four-parameter (Peleg) relationships. A non-linear least square regression analysis was used to evaluate the models constants. The GAB model best fitted the experimental data. The isosteric heat of sorption was determined from the equilibrium adsorption data using the Clausius–Clapeyron equation. Isosteric heats of sorption were 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 temperatures (T_g) of spray dried tomato pulp conditioned at various water activities were determined by differential scanning calorimetry. A strong plasticizing effect of water on T_g was found with a large reduction of T_g when the moisture content increased. These data were satisfactory correlated by the Gordon and Taylor model.

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1. Introduction

For half a century scientists have realized that water activity (a_w) is more important to the quality and stability of foods than the total amount of water present. The water sorption isotherm is an important tool, especially in low moisture foods. It can be applied to optimize the drying or rehydration conditions and determine the stability of the product during storage. It is common to present sorption isotherms by mathematical models based on empirical and/or theoretical criteria. In the literature there is a long list of available isotherm models, which can be divided into several categories; kinetic models based on an absorbed

mono-layer of water (BET model) (Brunauer, Emmett, & Teller, 1938), kinetic models based on a multi-layer and condensed film (e.g. GAB model, Van den Berg & Bruin, 1981), semi-empirical (e.g. Halsey model, Halsey, 1948) and purely empirical models (e.g. Oswin and Smith models, Oswin, 1946; Smith, 1947).

The thermodynamic properties of foods provide an understanding of water properties and energy requirements associated with the sorption behavior. Differential heat of sorption, often referred as isosteric heat of sorption, is used as an indicator of the state of water adsorbed by the solid particles and its knowledge is important when designing equipment for dehydration processes. The differential entropy of a material is proportional to the number of available sorption sites at a specific energy level, whereas Gibbs free energy is indicative of the affinity of sorbents for water and provides a criterion whether water sorption

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occurs as a spontaneous process (Telis, Gabas, Menegalli, & Telis-Romero, 2000).

Recently, the concepts related to water activity have been enriched by those of glass transition temperature (T_g), thus providing an integrated approach to the role of water in food. T_g defines a second-order phase change temperature at which a solid “glass” is transformed to a liquid-like “rubber”. As the temperature increases above T_g various changes, such as increase of free volume, decrease of viscosity, increase of specific heat, and increase of thermal expansion, are noticed. The most important changes affecting food behavior are related to the exponential increase of molecular mobility and decrease of viscosity. These factors govern various time-dependent and often viscosity related structural transformations, such as stickiness, collapse, and crystallization during food processing and storage. The importance of T_g of amorphous food materials for processing and storage stability has been recognized and emphasized by many researchers and a wide range of potential food applications of the glass transition phenomenon have been identified (Matveev, Grinberg, & Tolstoguzov, 2000; Moraga, Martinez-Navarrete, & Chiralt, 2006; Roos, Karel, & Kokini, 1996).

Fresh tomato and tomato products have aroused new scientific interest in the last few years. Among the various tomato products, powder enjoys a specialist market. Tomato solids in powder form have many advantages, including ease of packing, transportation, and mixing. Tomato powder may be produced by various means but, due to the high proportion of pulpy material in tomato juice, vacuum drying methods are not highly successful and drum drying and various spray drying techniques are used to produce the most powder at the present time. However, tomato pulp is a product that is difficult to spray dry, as the powder tends to become soft and sticky while still warm, and poses a caking problem due to its hygroscopic and thermoplastic behavior (Goula & Adamopoulos, 2003). In previous work, an experimental spray dryer was modified for drying tomato concentrate. The modification made to the original dryer design consisted of connecting the spray dryer inlet air intake to an absorption air dryer. The modified spray drying system proved advantageous over the standard laboratory spray dryer. Preliminary air dehumidification improved not only product recovery, but, also product properties (Goula & Adamopoulos, 2005a; Goula & Adamopoulos, 2005b).

Both water activity and glass transition have been used extensively in the literature to evaluate the storage stability. According to Sablani, Kasapis, and Rahman (2007), a product is most stable at its monolayer moisture content, i.e. a water activity value of about 0.1–0.3, or at or below the corresponding glass transition temperature. Moisture sorption data have been reported for several foods (Akanbi, Adeyemi, & Ojo, 2006; Chen & Jayas, 1998; Kim, Song, & Yam, 1991; Maroulis, Tsami, Marinos-Kouris, & Saravacos, 1988; McLaughlin & Magee, 1998). In addition, thermodynamic properties data for various foodstuffs are abundant in litera-

ture including: potato, carrot, tomato, green pepper, and onion slices (Kiranoudis, Maroulis, Tsami, & Marinos-Kouris, 1993), starch powders (Al-Muhtaseb, McMinn, & Magee, 2004b), cereal grains (Tolaba, Suarez, & Viollaz, 1997), cassava and melon seeds (Aviara & Ajibola, 2002), garlic (Madamba, Driscoll, & Buckle, 1996), rice (Benado & Rizvi, 1985), and sugar beet root (Iglesias, Chirife, & Viollaz, 1976). However, moisture sorption and thermodynamics data for spray dried tomato pulp were not found in the literature. As far as glass transition temperature is concerned, state diagrams have been reported for apple slice (Bai, Rahman, Perera, Smith, & Melton, 2001), grape slice (Sa & Sereno, 1994), strawberry (Moraga, Martinez-Navarrete, & Chiralt, 2004), freeze-dried pineapple (Telis & Sobral, 2001), mango powder (Ayala, Walter, Martinez-Monzo, Fito, & Chiralt, 2002), freeze-dried persimmon (Sobral, Telis, Habitante, & Sereno, 2001), freeze-dried kiwifruit (Moraga et al., 2006), carrot (Georget, Smith, & Waldron, 1999), freeze-dried onion (Sa & Sereno, 1994), freeze-dried tomato cubes, and air-dried tomato halves (Telis & Sobral, 2002), but no data were found for spray dried tomato pulp.

Thus, the objective of this work was to provide experimental data for the sorption characteristics of spray dried tomato pulp in order to model the sorption isotherms using selected equations and to define the glass transition temperature, water activity and water content relationships.

2. Materials and methods

2.1. Spray drying of tomato pulp

A Buchi mini spray dryer (Model 191) was employed for the spray drying process. A peristaltic pump pumped tomato pulp to the atomizer, and atomization was performed using a two-fluid nozzle (inside diameter 0.5 mm), which used compressed air. The modification made on the original design consisted of connecting the spray dryer inlet air intake nipple to an air drying unit by a flexible plastic air duct. The compressed air was also dehumidified before its supply to the two-fluid nozzle. An Ultrapac 2000 adsorption dryer (Model 0005) with two desiccant cartridges was used to dry the air down to 0.01 g of water per kg of dry air. The atomizer pressure, the feed temperature, and the feed rate were 5 ± 0.1 bar, 32.0 ± 0.5 °C, and 1.75 ± 0.05 g/min, respectively, whereas the feed was medium concentrated tomato pulp with a constant total solids mass concentration of $14 \pm 0.05\%$, containing $1.40 \pm 0.02\%$ insoluble solids, $5.61 \pm 0.07\%$ sugars, $1.53 \pm 0.03\%$ acid, $2.20 \pm 0.02\%$ protein, and $1.10 \pm 0.01\%$ salt. Tomato pulp was spray dried with an air inlet temperature of 130 °C (± 1 °C), drying air flow rate of 22.75 m³/h (± 0.18 m³/h), and atomizing agent flow rate of 600 l/h (± 20 l/h).

2.2. Determination of sorption isotherms

The equilibrium moisture content of tomato powder was determined by a gravimetric technique at seven relative

humidities selected between 1% and 90% and at six temperatures between 20 and 70 °C. Sulphuric acid solutions were used to maintain the specified relative humidity inside the desiccators (Ruegg, 1980).

Tomato powder samples (3 ± 0.001 g) were placed in previously weighed aluminum dishes and dried at 45 °C in an air-circulated oven over silica gel for 3 days. The samples were subsequently kept in desiccators over sulphuric acid solutions of known relative humidity. A test tube containing thymol was placed inside the desiccators with high RH to prevent mold growth during storage. The desiccators were placed in temperature-controlled cabinets maintained at 20, 30, 40, 50, 60, or 70 °C (± 1 °C) and the samples were allowed to equilibrate until there was no discernible weight change (± 0.001 g). This involved a period of approximately three weeks. The total time for removal, weighing, and putting back the samples in the desiccators was about 30 s. This minimized the degree of atmospheric moisture sorption during weighing. The equilibrium moisture content was determined by drying in an oven at 70 °C until constant weight. All measurements were done in triplicate and additional parallels were analysed if the individual values from the triplicates deviated more than 0.6% from the triplicate mean.

2.3. Measurement of glass transition temperature

Tomato powder samples of about 1 g (± 0.01 g) were conditioned at 25 °C using sulphuric acid solutions to maintain the water activity level between 0.04 and 0.55, according to sorption isotherm methodology. After equilibrium was reached, samples of about 10 mg were taken for differential scanning calorimetry (DSC) analysis and the remaining material was analyzed for moisture content by drying at 70 °C. The glass transition temperature was determined by DSC, with a Perkin–Elmer Pyris 1 differential scanning calorimeter supplied with proper software. The samples were heated at 10 °C/min between –60 °C and 80 °C in an inert atmosphere. Preliminary runs with 2 and 5 °C/min heating rates gave virtually the same results, so the 10 °C/min rate was chosen for convenience. The reference was an empty pan, while liquid nitrogen was used for sample cooling before the runs. The mid point of the glass transition was considered as the characteristic temperature of the transition. All measurements were done in triplicate.

2.4. Data analysis

2.4.1. Sorption isotherms

The isotherm models used to fit the data are presented in Table 1. A non-linear least square regression analysis was used to determine the model parameters and the goodness of the fit of each model was evaluated by calculating the mean relative percentage deviation modulus, M_e , defined as

Table 1

Isotherm models used for experimental data fitting

Model	Mathematical expression
GAB (Van den Berg & Bruin, 1981)	$X = X_m C K a_w / [(1 - K a_w)(1 - K a_w + C K a_w)]$ (1)
BET (Brunauer et al., 1938)	$X = X_m C a_w / [(1 - a_w)(1 + (C - 1)a_w)]$ (2)
Halsey (Halsey, 1948)	$X = [-A / (T \ln a_w)]^{1/B}$ (3)
Smith (Smith, 1947)	$X = A + B \log(1 - a_w)$ (4)
Oswin (Oswin, 1946)	$X = A [a_w / (1 - a_w)]^B$ (5)
Peleg (Peleg, 1993)	$X = K_1 a_w^{n_1} + K_2 a_w^{n_2}$ (6)

Nomenclature: X : moisture content (% dry basis); X_m : monolayer value (% dry basis); T : temperature (K); $C, K, A, B, K_1, K_2, n_1, n_2$: constants (–).

$$M_e = \frac{100}{N} \sum_{i=1}^N \frac{|m_i - m_{pi}|}{m_i} \quad (7)$$

where m_i is the experimental value, m_{pi} is the predicted value, and N is the population of experimental data.

The GAB model contains three constants, which have physical meaning and are functions of temperature:

$$C = C_0 \exp(\Delta H_C / RT) \quad (8)$$

$$K = K_0 \exp(\Delta H_K / RT) \quad (9)$$

$$X_m = X_{m0} \exp(q_m / RT) \quad (10)$$

where T is the absolute temperature, R is the universal gas constant, C_0, K_0, X_{m0} , and q_m are adjustable constants for the temperature effect and ΔH_C and ΔH_K are functions of the heat of water sorption (Maroulis et al., 1988):

$$\Delta H_C = H_m - H_n \quad (11)$$

$$\Delta H_K = \lambda - H_n \quad (12)$$

where H_m and H_n are the heats of sorption of the monolayer and the multilayer of the water respectively, and λ is the heat of condensation of pure water.

There are two methods of regression analysis for estimating the constants of the GAB equation from experimental moisture sorption data; the direct and the indirect method. In the direct regression method the six GAB constants $X_{m0}, C_0, K_0, q_m, \Delta H_C, \Delta H_K$ are estimated by substituting Eqs. (8)–(10) into Eq. (1). All the experimental data are used directly with the same weight. In the indirect or successive method, the three GAB constants X_m, C and K are estimated at each temperature by regression analysis of Eq. (1) and then the constants $X_{m0}, C_0, K_0, q_m, \Delta H_C, \Delta H_K$ are estimated by regression analysis of Eqs. (8)–(10). The experimental data are grouped at various temperatures for the first regression, and they are subsequently represented by derived values. The derived values may introduce significant uncertainties into the second, third and fourth regressions. Thus, the application of the indirect regression method depends very much on the confidence limits and regions of the constants X_m, C , and K that are obtained from the first approximation. According to Maroulis et al. (1988), the indirect non-linear regression method is not recommended since the basic three constants

of the GAB equation are interrelated. Thus, in this work the fit of the GAB equation to the water vapor adsorption data of the spray dried tomato pulp was studied using the direct regression.

2.4.2. Thermodynamic properties

The net isosteric heat of sorption can be determined from Eq. (13), which is derived from the Clausius–Clapeyron equation, applied to the system and pure water with the following assumptions: (1) moisture content of the system remains constant and (2) heat of vaporization of pure water and excess heat of sorption do not change with temperature (Al-Muhtaseb et al., 2004b)

$$\left. \frac{\partial \ln(a_w)}{\partial(1/T)} \right|_X = -\frac{q_{st}}{R} \quad (13)$$

where q_{st} is the net isosteric heat of sorption in J/mol, T is the absolute temperature in K, X is the equilibrium moisture content in kg/kg dry solid, and R is the universal gas constant (8.314 J/mol K).

The change in molar differential entropy can be calculated from Gibbs–Helmholtz equation (Telis et al., 2000):

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (14)$$

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 as

$$\Delta G = RT \ln a_w \quad (15)$$

Substituting Eq. (15) in Eq. (14) and rearranging:

$$\ln a_w = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \quad (16)$$

The enthalpy and entropy changes can be calculated from Eq. (16) by plotting the sorption isotherm in the form of $\ln(a_w)$ versus $1/T$ for certain values of the material moisture content and then determining the slope ($-\Delta H/R$) and the intercept ($\Delta S/R$). The net isosteric heat of sorption is determined by applying Eq. (13). This approach assumes that q_{st} is invariant with temperature, with the application of the method requiring measurement of sorption isotherms at more than two temperatures. An empirical exponential relationship between the isosteric heat of sorption and the moisture content has been proposed (Tsami, Marinou-Kouris, & Maroulis, 1990):

$$q_{st} = q_0 \exp(-X/X_0) \quad (17)$$

where q_0 is the isosteric heat of sorption of the first molecule of water in the food in J/mol, and X_0 is a characteristic moisture content of the food material in kg/kg dry solid, at which this isosteric heat of sorption has been reduced by 63%. The constants q_0 and X_0 are estimated by fitting Eq. (17) to the values of q_{st} , obtained by applying Eq. (13) to experimental isotherms.

A plot of ΔH versus ΔS from values of Eq. (16) can be evaluated for each set of sorption data. These values can be correlated according to the following equation:

$$\Delta H = T_B \Delta S + \Delta G_B \quad (18)$$

where T_B denotes the isokinetic temperature, which represents the temperature at which all reactions in the sorption series proceed at the same rate. Since there is a high degree of linear correlation between enthalpy and entropy, the compensation theory can be assumed to be valid for sorption. Krug, Hunter, and Grieger (1976) recommended a test for the compensation theory, which involves comparing the isokinetic temperature with the harmonic mean temperature, T_{hm} , which is defined as

$$T_{hm} = \frac{n}{\sum_{i=1}^n (1/T)} \quad (19)$$

where n is the number of isotherms.

A linear chemical compensation pattern exists only if $T_B \neq T_{hm}$. If $T_B > T_{hm}$ the process is enthalpy driven, while if the opposite condition is observed, the process is considered to be entropy-controlled.

2.4.3. Water plasticization behavior

To predict the plasticization effect of water, glass transition temperature and moisture content data were fitted to the model proposed by Gordon and Taylor (1952):

$$T_g = \frac{(1 - x_w)T_{gs} + kx_w T_{gw}}{(1 - x_w) + kx_w} \quad (20)$$

where T_g , T_{gs} , T_{gw} are the glass transition temperatures of the mixture, solids, and water, respectively, x_w is the mass fraction of water and k is the Gordon–Taylor parameter.

The relationship between glass transition temperature and water activity was modeled by an empirical model developed by Khalloufi, El-Maslouhi, and Ratti (2000):

$$T_g = \frac{Ca_w^2 + Da_w + E}{ca_w^2 + da_w + 1} \quad (21)$$

where T_g is the glass transition temperature in K and C , D , E , c , and d are model parameters.

3. Results and discussion

3.1. Sorption isotherms

The experimental moisture sorption data for tomato powder at 20, 30, 40, 50, 60, and 70 °C are shown in Fig. 1. The sorption isotherms demonstrate an increase in equilibrium moisture content with increasing water activity, at constant temperature, and are sigmoid in shape for most of the examined temperatures, characteristic of amorphous materials rich in hydrophilic components (Al-Muhtaseb, McMinn, & Magee, 2004a). At low and intermediate water activities, the so-called multilayer sorption region, moisture content increases linearly with a_w , whereas at high water activity levels, the so-called capillary condensation

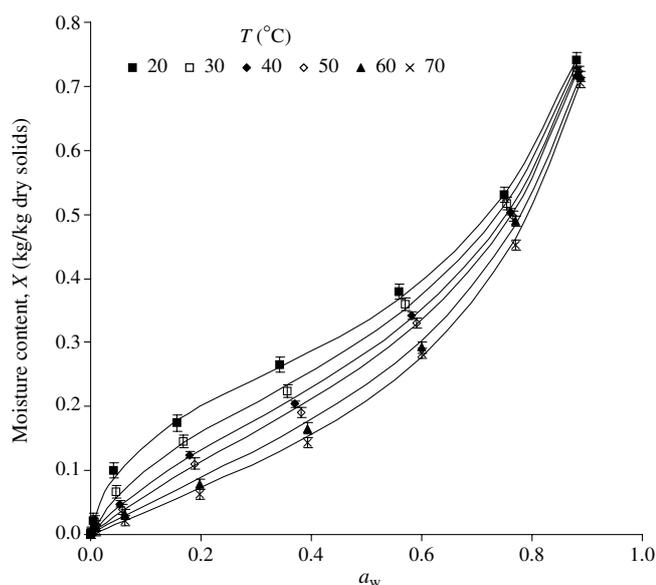


Fig. 1. Sorption isotherms of spray dried tomato pulp at various temperatures – experimental (symbols) and predicted by the GAB model (lines).

region, water content rapidly increases with a_w . The explanation for the nature of the isotherms may be that, at low water activities, physical sorption on strongly active sites of proteins occurs, since water can be sorbed only to surface – OH sites of crystalline sugar. Moreover, according to Falade and Aworh (2004), at low a_w it is possible to have a local dissolution of sugar alcohols, a swelling of proteins and appearance of new active sites. In the intermediate a_w range, sorption takes place at less active sites and, from this point on, there is gradual dissolution of sugars resulting in a complete exudation of sugars in solution at high water activities. However, sorption isotherm of tomato powder follows the type II BET classification shape, and not the type I, which is usual for high sugar foods. This observation may be attributed to the high protein content of spray dried tomato pulp.

The isotherms of many foods at room temperature are known. However, few investigations have been conducted to determine isotherms at temperatures higher than room temperature, and in many of these works the effect of temperature on the a_w of the saturated salt solutions, used to control the relative humidity, is not accounted, so errors in subsequent computations are introduced. Generally, the effect of temperature on the sorption isotherm is of great importance given that foods are exposed to a range of temperatures during storage and processing, and water activity changes with temperature for the same moisture content. Temperature affects the mobility of water molecules and the dynamic equilibrium between vapor and adsorbed phases. Experimental data indicate that the equilibrium moisture content decreases with increasing temperature, at a constant water activity. This trend may be attributed to a reduction in the total number of active sites

for water binding as a result of physical and/or chemical changes induced by temperature. According to Palipane and Driscoll (1992), at increased temperatures water molecules get activated to higher energy levels and break away from the water-binding sites of the food, thus decreasing the equilibrium moisture content. However, many researchers reported that the presence of large quantities of crystalline sugar, such as glucose, in dry foods can cause a different effect of temperature at high a_w levels. Myhara and Sablani (2001) reported that the equilibrium moisture content of high glucose raisin or date at a_w up to 0.55 decreases as the temperature increases, whereas at higher water activity levels increases sharply as the temperature increases. However, in the sorption isotherms presented in Fig. 1, the temperature effect is not dependent on a_w level. This may be due to the fact that tomato powder contains high levels of protein and insoluble solids.

The typical sigmoid curves of sorption isotherms predicted by the GAB model are also shown in Fig. 1. The fit of the GAB equation to the water vapor adsorption data of the spray dried tomato pulp was performed using the direct regression approach. The results are shown in Table 2. Considering the values for R^2 and M_e the GAB equation can be considered satisfactory for fitting the adsorption of tomato powder. Maximum, minimum, and average values for X_m , C and K were calculated using the estimated constants X_{m0} , C_0 , K_0 , q_m , ΔH_C , ΔH_K (Table 2). Estimated values for X_m are within the reported values for vegetables, which vary between 18% and 22% (dry basis) and were found to be greater than those for fruits, which vary between 10% and 15% (dry basis) (Kiranoudis et al., 1993). The monolayer moisture content X_m is recognized as the moisture content affording the longest time period with minimum quality loss at a given temperature. Below it, rates of deteriorative reactions, except oxidation of unsaturated fats, are minimal. Therefore, at a given temperature, the safest water activity level is that corresponding to X_m or lower. The safest a_w values corresponded to

Table 2

Fitting of the GAB model to the water vapor adsorption for the spray dried tomato pulp

Mean coefficient of determination (R^2)	0.996
Mean relative percentage deviation modulus (M_e), %	3.49
Constant X_{m0} , % dry basis	13.82
Constant q_m , kJ mol ⁻¹	1.06
Maximum X_m , % dry basis	21.32
Minimum X_m , % dry basis	20.04
Average X_m , % dry basis	20.64
Constant C_0	6.10×10^{-6}
Heat related to monolayer water (ΔH_C), kJ mol ⁻¹	36.08
Maximum C	18.83
Minimum C	1.95
Average C	7.09
Constant K_0	1.062
Heat related to multilayer water (ΔH_K), kJ mol ⁻¹	0.641
Maximum K	0.848
Minimum K	0.816
Average K	0.833

X_m for spray dried tomato pulp were predicted using data in Table 2 and are tabulated in Table 3.

The values for C are also within the reported limits for vegetables and values for K are smaller than 1 as dictated by the GAB equation. Parameter ΔH_C is the difference in enthalpy between monolayer and multilayer sorption, which is expected to have a large positive value, due to the strong exothermic interaction of water vapor with primary sorption sites of the material. The estimated value of ΔH_C is also in agreement with values reported for various vegetables, which were found to be greater than those for fruits (Maroulis et al., 1988). Parameter ΔH_K is the difference between the heat of condensation of water and the heat of sorption of a multimolecular layer. The estimated value was found to be positive but small which is in agreement with the literature (Samaniego-Esguerra, Boag, & Robertson, 1991; Tsami et al., 1990).

Giovanelli, Zanoni, Lavelli, and Nani (2002) also used the GAB equation to model experimental sorption data reported for freeze dried tomato pulp, freeze dried insoluble solids-rich tomato, and air dried tomato halves. The relevant sorption isotherms at 20 °C are shown in Fig. 2 along with those for spray-dried tomato. Freeze-dried insoluble solids-rich tomato was the least hygroscopic of all dried products. This may be due to the removal of sol-

uble solids, such as glucose and fructose, by the centrifugation used to separate the tomato serum. According to Giovanelli et al. (2002), this product requires higher water removal during drying to reduce water activity and is more sensitive to moisture variations during storage. In addition, at low and medium water activities the water contents of freeze dried pulp and air dried halves were lower than that of spray dried pulp, whereas at high a_w levels freeze and air dried products showed a rapid increase in their water content. Generally, monosaccharides exhibit a long flat segment in their sorption isotherm within the a_w range of 0.1–0.6 and rapid increases in their water content at a_w levels above 0.6–0.8 (Biliaderis, Lazaridou, & Arvanitoyannis, 1999). In contrast, the other tomato constituents absorb water even at low a_w levels. Thus, a feasible explanation for the lower water uptake of freeze and air dried products at low water activity is that the modified spray drying system achieved extremely low drying temperatures (Goula & Adamopoulos, 2005a) preventing thermal degradation of various tomato constituents that adsorb water. Conversely, at high a_w levels, where primarily sugars adsorb water, freeze dried pulp and air dried halves were more hygroscopic than spray dried powder, as they were characterized by a higher sugar content level, as a result of their production method.

The parameters for other sorption models are presented in Table 4, along with the mean relative M_e . The GAB model gives M_e values ranging from 3.1% to 4.0% with an average value of 3.5% and best describes the experimental adsorption data throughout the entire range of water activity. This observation is similar to that obtained by other researchers, who studied sorption isotherms of various fruits and vegetables. Kiranoudis et al. (1993) determined the equilibrium moisture content of potato, carrot, tomato, green pepper, and onion within the range of 10–90% relative humidity and at three different temperatures (30, 45, and 60 °C) and found the GAB model satisfactory for the prediction of the experimental data obtained. McLaughlin and Magee (1998) determined the sorption isotherms for potatoes at temperatures of 30, 45, and 60 °C and, among the models tested, the GAB model gave the best fits. According to Al-Muhtaseb et al. (2004a), the GAB model adequately represented the sorption isotherms of potato and wheat starch, whereas Akanbi et al. (2006) concluded that equilibrium moisture contents of tomato slices obey closely the GAB equation.

Only experimental data with $a_w < 0.50$ were fitted to the BET model, because above that value the model hypothesis fails and the equation is not able to predict sorption behavior accurately. One of the two BET constants, X_m , is, as in the GAB equation, the monolayer capacity. The values of X_m ranging from 14.6% to 19.0% (dry basis) were within the reported values for vegetables (Tsami et al., 1990) and lower than that obtained by the GAB model. Despite the theoretical limitations of the BET adsorption analysis, the monolayer value was found to be a reasonable guide with respect to various aspects of interest in dried foods.

Table 3
Monolayer moisture content (X_m) and corresponding a_w for spray dried tomato pulp

Temperature (°C)	Monolayer moisture content, X_m (% dry basis)	a_w
20	21.3	0.23
30	21.1	0.30
40	20.7	0.35
50	20.5	0.39
60	20.2	0.44
70	20.0	0.49

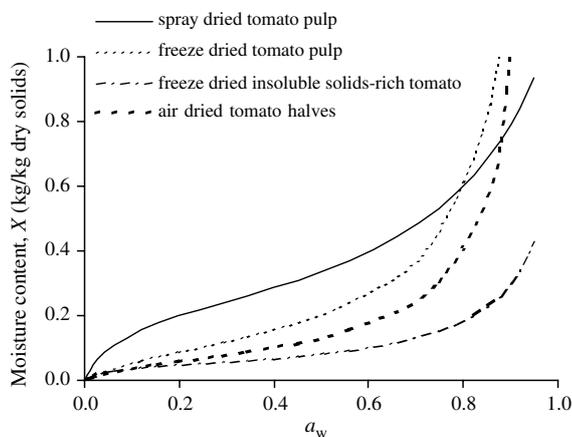


Fig. 2. Water sorption isotherms (20 °C) modeled by the GAB equation for various dry tomato products. The dotted lines are based on data by Giovanelli et al. (2002).

Table 4
Parameters of the isotherm models for spray dried tomato pulp

Model	Constant	Temperature (°C)					
		20	30	40	50	60	70
GAB	X_m (% dry basis)	21.31	21.02	20.71	20.53	20.21	20.04
	C	18.83	8.85	5.76	4.30	2.85	1.95
	K	0.816	0.823	0.830	0.836	0.842	0.848
	M_e (%)	3.82	3.95	3.13	3.21	3.44	3.38
	Overall M_e (%)				3.49		
BET	X_m (% dry basis)	18.96	16.24	15.58	14.92	14.56	14.78
	C	19.04	14.06	8.18	6.11	3.37	2.03
	M_e (%)	3.40	10.40	9.43	8.75	19.93	17.22
	Overall M_e (%)				11.52		
Halsey	A	23.39	23.12	22.85	22.60	22.31	22.10
	B	1.80	1.69	1.57	1.50	1.40	1.33
	M_e (%)	86.14	61.55	50.78	45.90	39.63	36.31
	Overall M_e (%)				53.39		
Smith	A	0.067	0.049	0.032	0.020	0.006	−0.005
	B	−0.763	−0.754	−0.756	−0.759	−0.746	−0.722
	M_e (%)	58.30	30.11	23.61	18.91	30.06	42.91
	Overall M_e (%)				33.98		
Oswin	A	0.335	0.303	0.277	0.258	0.227	0.202
	B	0.402	0.441	0.483	0.515	0.567	0.603
	M_e (%)	24.87	13.78	8.58	10.03	18.25	25.56
	Overall M_e (%)				16.85		
Peleg	K_1	0.600	0.572	0.585	0.615	0.680	0.657
	K_2	0.465	0.416	0.436	0.440	0.351	0.541
	n_1	5.28	4.27	4.87	5.22	4.49	8.66
	n_2	0.54	0.60	0.75	0.85	0.89	1.40
	M_e (%)	8.07	1.89	7.12	6.98	11.36	9.34
	Overall M_e (%)				7.46		

The second parameter, C , is also an energy constant as the GAB constant, but with slightly different physical meaning (Moraga et al., 2006). It allows us to classify sorption isotherms according to Brunauer's classification. As the C values were higher than 2, the obtained sorption isotherms can be classified as type II. The Peleg model also adequately fitted the results with an average M_e value of 7.5%. Al-Muhtaseb et al. (2004a) also reported that the Peleg model provides a good description of the isotherms of potato starch, peas and cured beef and Lewicki (1998) determined the sorption isotherms of 31 food materials and found the Peleg model to show the best fit. The Halsey model gave the least accurate predictions, giving an average M_e value of 53.4%. Wang and Brennan (1991) and Al-Muhtaseb et al. (2004a) also reported that the Halsey model is inadequate for representing the sorption isotherms for various foods such as potato and starch powders. The Smith and Oswin models also failed to describe the experimental data accurately giving average M_e values of 34.0% and 16.9%, respectively.

3.2. Sorption thermodynamic properties

Water sorption in foods is a complex phenomenon. The main water-adsorbing constituents in foods are various polymers (proteins, starch, cellulose, hemicellulose, etc.)

and sugars. The different polar groups of the polymers provide energetically different sites for sorption. Besides, as a polymer sorbs water it undergoes changes of constitution, dimensions and other properties. Water sorption also leads to phase transformations of the sugars contained in the food. All these facts make the interpretation of the differential heat curves difficult; there are, however, some observations that could be made from the results. The net isosteric heat of water sorption at each moisture content was obtained by fitting Eq. (13) to the data of equilibrium water activity versus temperature, obtained from sorption isotherms. The results are shown in Fig. 3 and are similar to those presented by Kiranoudis et al. (1993), who reported a value of 42.9 kJ mol^{−1} for tomato slices at a moisture content of 12% (dry basis) falling to 7.4 kJ mol^{−1} at 36% (dry basis). In addition, the net isosteric heat of sorption remained significant for a wide range of values of material moisture content. This observation is in agreement with Tsami (1991) and Kiranoudis et al. (1993), who stated that in the case of vegetables, the net isosteric heat of desorption was large for moisture contents between 6% and 36% (dry basis), while in the case of fruits, it was found negligible over this range of moisture content, and only increased dramatically when the material moisture approached zero. Moreover, in the case of fruits the heat of sorption was found to be slightly negative at high moisture content,

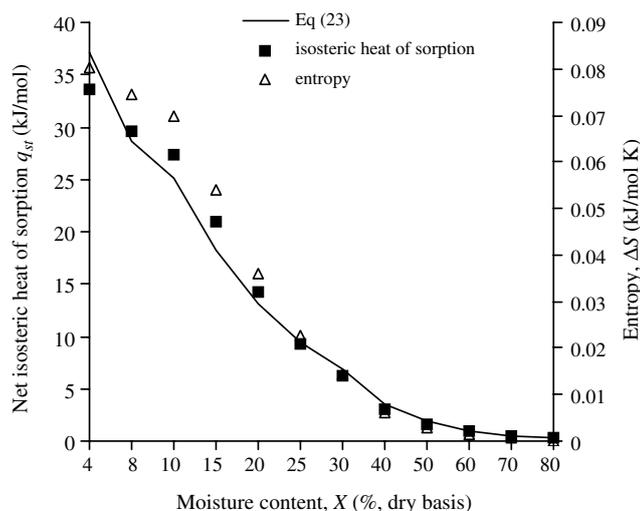


Fig. 3. Isosteric heat of sorption and entropy for spray dried tomato pulp at various moisture contents.

due to the contribution of the endothermic dissolution of sugars in the sorbed water, a phenomenon that was not observed in the case of spray dried tomato pulp.

Fig. 3 clearly illustrates a progressive increase in the heat of sorption with decreasing moisture content. At high moisture content the heat of sorption approaches zero, meaning that the heat of sorption is equal to the heat of vaporization of water. The effect of moisture content on heat of sorption was fitted by:

$$q_{st} = 48.25 \exp(-X/15.36) (R^2 = 0.982) \quad (22)$$

where X is the moisture content in % dry basis and q_{st} is the isosteric heat of sorption in kJ mol^{-1} . Similar effects of moisture content on the heat of sorption were reported by Mazza and LeMaguer (1978) for yellow globe onion, Saravacos, Tsiourvas, and Tsami (1986) for sultana raisins, Tsami (1991) for dried currants, figs, prunes, and apricots, Telis et al. (2000) for persimmon skin and pulp, and Al-Muhtaseb et al. (2004b) for starch powders. The physical explanation for the rapid increase in q_{st} at low moisture contents may be that in the initial stages of sorption there are highly active polar sites on the surface of the food material, which are covered with water molecules to form a monomolecular layer.

From the straight lines calculated by Eq. (16) at different moisture contents the values of ΔS were obtained (Fig. 3). The results showed a strong dependence of differential entropy on moisture content with an exponential trend similar to that exhibited by differential enthalpy. This observation is similar to that obtained by Al-Muhtaseb et al. (2004b), who studied the water sorption thermodynamic properties of starch powder. A plot of enthalpy versus entropy showed a linear correlation:

$$\Delta H = 395.670 \cdot \Delta S + 0.331 \quad (R^2 = 0.998) \quad (23)$$

As the law of compensation could be applied in the range of moistures studied, the results were correlated in accordance with Eq. (24) and the isokinetic temperature of sorp-

tion was found to be $T_B = 396 \text{ K}$. The harmonic mean temperature was calculated as $T_{hm} = 317 \text{ K}$, a value significantly different from the value of T_B , confirming the suitability of the isokinetic theory for water sorption in spray dried tomato pulp and since $T_B > T_{hm}$, the process can be characterized as enthalpy driven.

3.3. Water plasticization behavior

Representative DSC traces obtained with the sample conditioned at $a_w = 0.25$ are shown in Fig. 4. Similar curves were obtained for the samples conditioned at the other a_w levels. These curves are similar to those determined by other authors in other fruits and vegetables in the same domain of a_w (Telis & Sobral, 2001; Telis & Sobral, 2002). Generally, the thermograms obtained showed the typical second-order transition, the glass transition of the amorphous materials that produce a step change in the heat flow due to changes in heat capacity at the temperature of phase transition. Values of T_g obtained for the different samples as a function of moisture content are shown in Fig. 5. T_g values were slightly lower than that obtained by Telis and Sobral (2002) for air dried and freeze dried tomato halves, which had lower NaCl and citric acid content. Glass transition temperature is known to decrease with decreasing molecular weight (Roos et al., 1996; Slade & Levine, 1995), in such a way that higher NaCl and citric acid could have caused the observed decrease in T_g . According to Telis and Sobral (2002), T_g values of air dried tomato halves, especially those corresponding to osmotically pre-treated ones, were lower than that observed for freeze dried material at the same moisture content. In that case the lower T_g values were attributed to gained solutes, NaCl and sucrose.

Fig. 5 shows that the water plasticization effect causes a significant decrease of the glass transition temperature with increase in moisture content. This observation is similar to that obtained by other researchers, who studied glass transitions and state diagrams for various fruits and vegetables

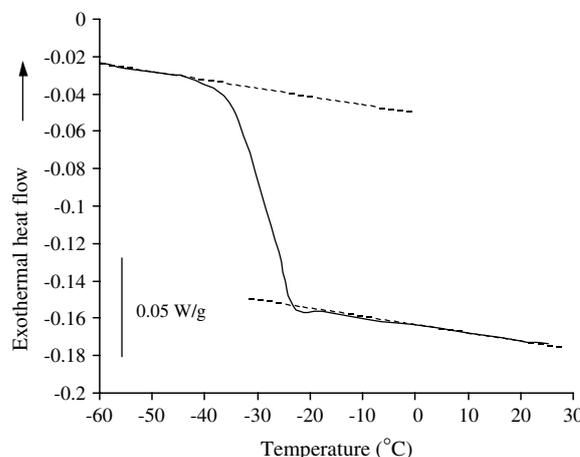


Fig. 4. DSC profile for tomato powder conditioned at a_w of 0.25.

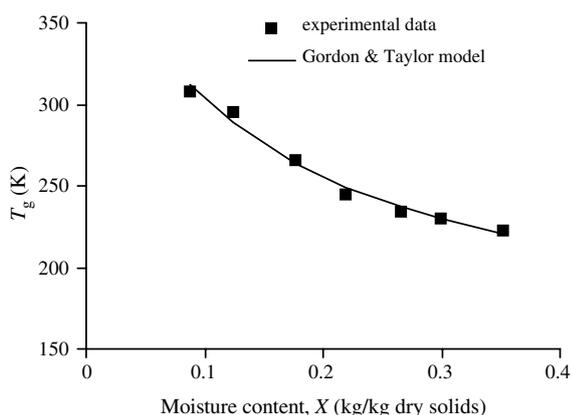


Fig. 5. Experimental (symbols) and predicted by Gordon and Taylor model (line) data for the relationship between glass transition temperature (T_g) and moisture content (X) of spray dried tomato pulp.

(Sa & Sereno, 1994). Telis and Sobral (2001) determined the glass transition temperatures of freeze dried pineapple conditioned at various water activities and concluded that for water activities lower than 0.90, the plasticizing effect of water on the T_g was evident, with a great reduction of T_g caused by increasing moisture content. Sobral et al. (2001) studied the phase diagram for freeze dried persimmon and observed that in the hygroscopic domain ($a_w < 0.90$), the plasticizing effect is clear, whereas at water activities higher than 0.90, the glass transition curve exhibits a discontinuity, with a sudden increase of T_g that approaches a constant value. This plasticizing 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. One more contributory factor is the low T_g of amorphous water, since this difference in T_g between water and food macromolecules decreases the viscosity of biopolymer–water mixtures over a wide range of temperatures.

The Gordon and Taylor model has proved to be a reliable predictor of glass transition temperatures of sugars at various water contents and has been used in several fruit and vegetable samples that can be considered as binary mixtures of solids and water. It was fitted to experimental points using $T_{gw} = 138$ K, with the following parameters calculated by non-linear regression: $T_{gs} = 412.8$ K and $k = 6.69$, with $R^2 = 0.985$. Fig. 5 shows the curve predicted by Gordon and Taylor model. The calculated k value was similar to those reported for fruits and sugar solutions (Khalloufi et al., 2000; Moraga et al., 2004). Telis and Sobral (2002) fitted glass transition temperature–moisture content data for freeze dried and air dried tomato to the model proposed by Gordon and Taylor and found T_{gs} and k values of 603.9 K and 9.35, respectively. This difference in the values of Gordon and Taylor parameters can be attributed to differences in composition (mean molecular weight of the solutes) of the tomato liquid phase.

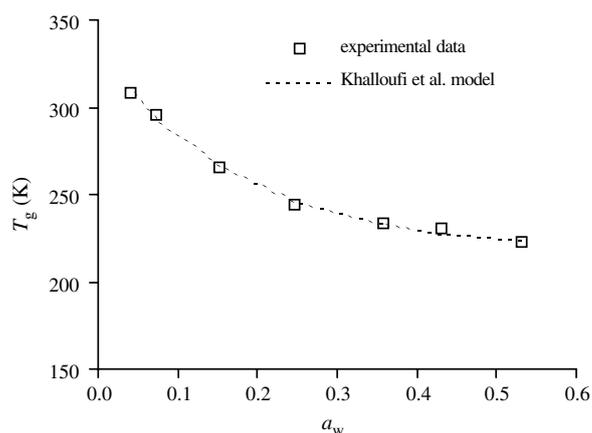


Fig. 6. Experimental (symbols) and predicted by Khalloufi et al. model (line) data for the relationship between glass transition temperature (T_g) and a_w for spray dried tomato pulp.

Another relationship of interest in the prediction of the physical state in food materials is given in Fig. 6, which presents a plot of T_g data against a_w . This relationship was modeled by the empirical model developed by Khalloufi et al. (2000):

$$T_g = \frac{744.17a_w^2 + 516.38a_w + 335.25}{2.44a_w^2 + 3.71a_w + 1} \text{ (K)} \quad (R^2 = 0.993) \quad (24)$$

This equation allows for a rapid and reliable method for calculating the T_g for spray dried tomato pulp stored under specific relative humidity conditions. Fig. 5 allows us to obtain the critical water content at which, at a specific storage temperature, the glass transition occurs. If the product is commercialized at 25 °C, the critical value of water content at which the product “glass” is transformed to a liquid-like “rubber” is 10.7% dry basis. Above this value, tomato powder becomes sticky and the crystallization of amorphous compounds could take place. This critical value is lower than the monolayer moisture content, thus indicating that the X_m is not a water content that assures quality preservation during storage of spray dried tomato pulp.

4. Conclusions

On the basis of this work the following conclusions can be drawn:

- The moisture sorption isotherms of tomato pulp spray dried in dehumidified air follows a sigmoid isotherm curve typical of the type II BET classification shape.
- Temperature affects the sorption behaviour; the equilibrium moisture content decreases with increasing temperature, at constant water activity.
- Within the temperature range investigated, the kinetic three-parameter GAB model and the empirical four-parameter Peleg equation were found to best represent the experimental data throughout the entire range of water activity.

- An exponential relation was found to adequately describe the dependence of isosteric heat of sorption on the equilibrium moisture content.
- Water acts as a plasticizer in spray dried tomato pulp decreasing its glass transition temperature and the Gordon and Taylor model could adequately represent the sugar matrix glass transition curve.

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