Original article

Moisture sorption isotherms and thermodynamic properties of apple Fuji and garlic

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Summary The moisture equilibrium isotherms of garlic and apple were determined at 50, 60 and 70 °C using the gravimetric static method. The experimental data were analysed using GAB, BET, Henderson–Thompson and Oswin equations. The isosteric heat and the differential entropy of desorption were determined by applying Clausius–Clapeyron and Gibbs–Helmholtz equations, respectively. The GAB equation showed the best fitting to the experimental data ($R^2 > 99\%$ and $E\% < 10\%$). The monolayer moisture content values for apple were higher than those for garlic at the studied temperatures; the values varied from 0.050 to 0.056 and from 0.107 to 0.168 for garlic and apple, respectively. The isosteric heat and the differential entropy of desorption were estimated in function of the moisture content. The values of these thermodynamic properties were higher for apple (in range 48–100 kJ mol^{-1} and 14–150 J mol^{-1} K^{-1}) than for garlic (in range 43–68 kJ mol^{-1} and 0–66 J mol^{-1} K^{-1}). The water surface area values decreased with increasing temperature. The Kelvin and the Halsey equations were used to calculate the pore size distribution.

Keywords Apple, drying, fruits/vegetables, garlic, physicochemical properties.

Introduction

Garlic (*Allium sativum)* has been cultivated for centuries all over the world on account of its culinary and medicinal properties. Garlic is dehydrated into different products such as powders, flakes and slices. Dehydrated garlic has great commercial value and is used as a spice or standard ingredient in prepared foods and formulations (Pezzutti & Crapiste, 1997). Apple cultivation is a relevant economic activity in south region of Brazil, being that cultivates Fuji and Gala constitutes about 95% of the Brazilian production (Wosiacki *et al*., 2004). The apples are consumed either fresh or in the form of various processed products such as juice, jam, marmalade and dried (Sacilik & Elicin, 2006).

The knowledge of the relationship between moisture content and water activity is essential for drying and storage. At the end of the drying process, the product moisture content reaches a value that corresponds to the equilibrium with the surrounding atmosphere and its mass becomes stationary. This thermodynamic equilibrium is characterised for the equilibrium isotherms, and its determination is essential for the better understanding of modelling problems on drying operations (Kouhila *et al*., 2001). Knowledge of the sorption equilibrium is also important for predicting stability and quality changes during packaging and storage of dehydrated foods and formulations (Pezzutti & Crapiste, 1997). The widely accepted criteria used to select the most appropriate sorption model were the degree of fit to the experimental data and the simplicity of the model (Simal *et al*., 2007).

Thermodynamic parameters such as isosteric heat and differential entropy of sorption determine the end-point to which food must be dehydrated in order to achieve a stable product with optimal moisture content, and yield the theoretical minimum amount of energy required to remove a given amount of water from the food. These parameters also provide an insight into the microstructure associated with the food as well as the theoretical interpretation of physical phenomena occurring at the food–water interface (Togrul & Arslan, 2007).

The isosteric heat of sorption is the required energy to remove water from the mass unit of a solid matrix. It can be considered an indicative of the intermolecular attraction forces between sorption sites and water. The change in the isosteric heat of sorption with the moisture content of the sample indicates the availability of polar sites to water vapour as desorption/adsorption proceeds (Kumar *et al*., 2005). The heat of sorption of water is important for modelling various food processes and

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food storage, as well as for designing the equipment of some processes (Delgado & Sun, 2002). The differential entropy of a material is proportional to the number of available sorption sites at a specific energy level (McMinn & Magee, 2003).

The Kelvin equation is the most commonly employed model for evaluation of the pore size distribution in porous materials with mesopores size, but it does not take into account the thickness of the layers formed on the porous surface prior to condensation. The Halsey equation has been studied by many researchers to predict the thickness of these layers (Lastoskie *et al.*, 1993).

The aims of the present study were to determine the equilibrium isotherms of garlic and apple at 50, 60 and 70 °C, to fit a suitable model for describing the sorption characteristics and to determine thermodynamic functions as the isosteric heat and the differential entropy of desorption, the surface area and the pores sizes distribution from experimental data.

Material and methods

Material

The utilised raw materials were garlic (*Allium sativum L.*) cultivar amarante and apple Fuji (*Mallus percicae*). The moisture analyses of samples were realised according to AOAC (1995) by the vacuum oven method.

Experimental procedure

Equilibrium moisture contents of samples were determined at 50, 60 and 70 °C. The static gravimetric method with sulphuric acid solutions at different concentrations was used. Initially, the samples of garlic and apple were peeled and cut uniformly in small pieces of c. (0.5 × 0.5 × 0.3) cm of size. The samples were put in glass jars. It was used as an initial mass of c. 3 g in each jar. Eleven jars were filled until a quarter depth with different concentrations of sulphuric acid solutions (20–70% p/p) to keep the water activity of 0.06–0.89 inside the jars, according to Perry (1984). The samples, placed on support in each jar, were not in contact with the acid solution. The jars were placed in an incubator with controlled temperature (± 1 °C) for c. 20 days. Samples were weighed at regular intervals and the equilibrium was judged to have been attained when the difference between three consecutive weighing did not exceed 0.001 g. When the equilibrium conditions were reached, the moisture content analysis was carried out. Each experiment was accomplished in triplicate.

Calculation procedure

Numerous mathematical models for the description of the moisture sorption behaviour of foods are available in the literature. Some of these models are based on theories of the mechanism of sorption, others have been purely empirical, or semi-empirical (Kaymak-Ertekin & Gedik, 2004). Al-Muhtaseb *et al.* (2002) reviewed moisture sorption characteristics of food products, and the applicability of various mathematical models was discussed. However, because of complex composition and structure of foods, mathematical prediction of sorption behaviour is difficult. Some of the mostly applied equations are GAB, BET, Henderson–Thompson and Oswin (Kaya & Kahyaoglu, 2007).

The GAB and the BET models have a theoretical basis, whereas the other models are empirical or semi-empirical (Adebowale *et al.*, 2007). The parameters of the GAB (eqn 1) and BET (eqn 2) models have a physical meaning. In the GAB and BET models, M_e is the equilibrium moisture content, a_w is the water activity, M_m is the water content corresponding to saturation of all primary sites by one water molecule (namely monolayer moisture content), and C_G, K and C_B are energy constants. The Henderson–Thompson (eqn 3) and the Oswin (eqn 4) equations are empirical models and a_1, a_2, b_1 and b_2 are constants. All equations are shown below.

$$M_e = \frac{M_m \cdot C_G \cdot K \cdot a_w}{(1 - K \cdot a_w) \cdot (1 - K \cdot a_w + C_G \cdot K \cdot a_w)} \quad (1)$$

$$M_e = \frac{M_m \cdot C_B \cdot a_w}{(1 - a_w) \cdot (1 - a_w + C_B \cdot a_w)} \quad (2)$$

$$M_e = \left[\frac{\ln(1 - a_w)}{-a_1}\right]^{1/b_1} \quad (3)$$

$$M_e = a_2\left(\frac{a_w}{1 - a_w}\right)^{b_2} \quad (4)$$

Non-linear regression analysis was done with the experimental data of equilibrium isotherms of garlic and apple, using the STATISTICA for Windows 5.1 (StatSoft, Inc., Tulsa, OK, USA), which estimates the parameters of eqns 1, 2, 3 and 4. The fit of different models to observations was evaluated with the determination coefficient (R^2) and mean relative error ($E\%$), which is defined in eqn 5.

$$E\% = \frac{100}{N}\left(\sum_{i=1}^{n} \frac{\left|M_e^i - M_p^i\right|}{M_e^i}\right) \quad (5)$$

where M_e^i is the experimental value, M_p^i is the predicted value and N is the number of experimental points.

The net isosteric heat of sorption can be determined from moisture sorption data using the equation derived from the Clausius–Clapeyron equation (eqn 6), and the isosteric heat of sorption was calculated by eqn 7 (Arslan & Togrul, 2005).

$$\frac{\mathrm{d}(\ln a_{\mathrm{w}})}{\mathrm{d}(1/T)} = -\frac{q_{\mathrm{st}}}{R} \tag{6}$$

$$Q_{\mathrm{st}} = q_{\mathrm{st}} + \Delta H_{\mathrm{vap}} \tag{7}$$

where a_{w} is the water activity, T is the temperature (K), q_{st} the net isosteric heat of sorption (kJ mol^{-1}), R is the universal gas constant (kJ mol^{-1} K^{-1}), Q_{st} the isosteric heat of sorption (kJ mol^{-1}) and ΔH_{vap} the heat of vaporisation of water (kJ mol^{-1} water).

The differential entropy of desorption (S_{d}) can be calculated from Gibbs–Helmholtz equation, as presented in eqn 8 (Simal *et al.*, 2007).

$$S_{\mathrm{d}} = \frac{q_{\mathrm{st}} - G}{T} \tag{8}$$

where the free Gibbs energy is calculated as:

$$G = RT \ln a_{\mathrm{w}} \tag{9}$$

Substituting eqn 9 in eqn 8, and after rearranging, the final form is eqn 10.

$$-\ln a_{\mathrm{w}} = \frac{-q_{\mathrm{st}}}{RT} - \frac{S_{\mathrm{d}}}{R} \tag{10}$$

where S_{d} is the differential entropy (kJ mol^{-1} K^{-1}), q_{st} is the net isosteric heat of sorption (kJ mol^{-1} K^{-1}), G is the free Gibbs energy (kJ mol^{-1}), R the universal gas constant (kJ mol^{-1} K^{-1}), T is absolute temperature (K) and a_{w} is the water activity.

The net isosteric heat (q_{st}) and differential entropy S_{d} of desorption can be calculated by plotting ln(a_{w}) vs. $1/T$, for a specific moisture content of the material, and determining the slope ($-q_{\mathrm{st}}/R$) and intercept (S_{d}/R). This procedure is repeated for many values of moisture content to determine q_{st} and S_{d} dependency with the moisture content (Delgado & Sun, 2002; Kaya & Kahyaoglu, 2007).

Specific surface area is an important role in determining the water-binding properties of particulate materials. The values of water surface area, given in m^2 g^{-1} of solid, can be determined from eqn 11, using the monolayer moisture values (Cassini *et al.*, 2006).

$$S_0 = M_{\mathrm{m}} \frac{1}{\mathrm{PM}_{\mathrm{H_2O}}} N_0 \mathrm{A}_{\mathrm{H_2O}} = 3.5 \times 10^3 M_{\mathrm{m}} \tag{11}$$

where S_0 is the surface area (m^2 g^{-1}), M_{m} is the monolayer moisture content, $\mathrm{PM}_{\mathrm{H_2O}}$ is the molecular weight of water (18 g mol^{-1}), N_0 is the number of Avogadro (6 × 10^{23} molecules per mole) and $\mathrm{A}_{\mathrm{H_2O}}$ is the area of water molecule (10.6 × 10^{-20} m^2).

The average pore size at any given moisture content was determined by the Kelvin and the Halsey equations. The Kelvin equation, eqn 12, is used for the calculation of critical radius (Singh *et al.*, 2001).

$$r_{\mathrm{c}} = \frac{2\sigma V_{\mathrm{M}}}{RT \ln(1/a_{\mathrm{w}})} \tag{12}$$

The thickness of the adsorbed layer of water was calculated from the Halsey equation (eqn 13).

$$t = 0.354 \times \left(\frac{-5}{\ln a_{\mathrm{w}}}\right)^{1/3} \tag{13}$$

Pore radius R_{p} is obtained by the sum of the critical radius r_{c}, and the multilayer thickness, t, showed in eqn 14.

$$R_{\mathrm{p}} = r_{\mathrm{c}} + t \tag{14}$$

where r_{c} is the critical radius (m), σ is the surface tension (N m^{-1}), V_{M} is the molar volume of sorbate (m^3 mol^{-1}), R is the universal gas constant (kJ mol^{-1} K^{-1}), T is the temperature (K), a_{w} is the water activity, t is the multilayer thickness (m) and R_{p} is the pore radius (m).

The volume values of the liquid (with relation to 1 kg of dry material) contained in the pores with a radius R_{p}, was calculated according to eqn 15.

$$V = M\frac{1}{\rho} \tag{15}$$

where V is the volume of liquid (m^3 kg^{-1} dried material), M is the moisture content and ρ is the density (kg m^{-3}).

Results and discussion

The initial moisture content values for the samples of garlic and apple were 1.94 ± 0.09 and 5.66 ± 0.41 g water per gram dry matter (dry basis), respectively.

Through the values of water activity (a_{w}) obtained from Perry (1984) and the experimental data of equilibrium moisture content (M_{e}) of the materials, at the three studied temperatures, was plotted the curves M_{e} vs. a_{w}, showed in Fig. 1 for garlic and in Fig. 2 for apple.

The sigmoid shapes of the isotherm curves at different temperatures, which are typical of food isotherms, can be observed in Figs 1 and 2. In the first segment (with low a_{w}) of the S-shaped sorption isotherm curves, garlic and apple adsorbed relatively lower amounts of moisture per unit increase in water activity. However, larger amount of moisture was adsorbed at higher a_{w}. Similar behaviour has been reported by other authors for different foods (Sanni *et al.*, 1997; McLaughlin & Magee, 1998; Togrul & Arslan, 2007). The data for garlic (Fig. 1) also indicate that the equilibrium moisture content decreased with increasing temperature, at constant a_{w}, thus indicating that the materials became

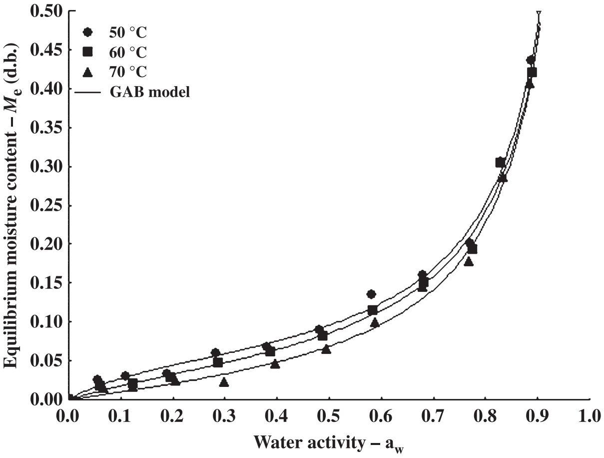

Figure 1 Sorption isotherms of garlic at different temperatures, utilising the GAB model.

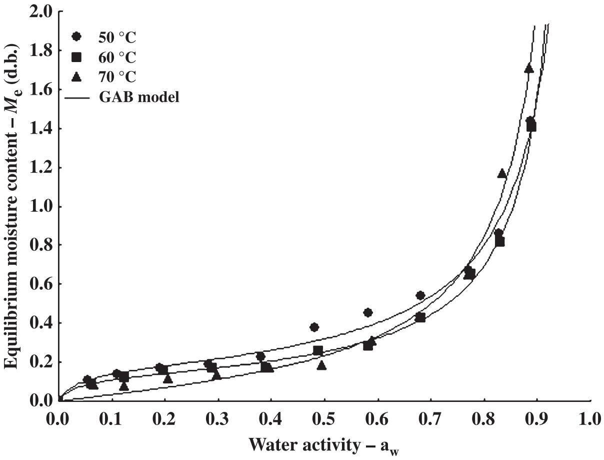

Figure 2 Sorption isotherms of apple at different temperatures, utilising the GAB model.

less hygroscopic. This trend may be due to a reduction in the total number of active sites for water-binding as a result of physical and/or chemical changes in the product induced by temperature.

In Fig. 2, the isotherms for apples present the same behaviour that the isotherms for garlic in low water activities range and then the isotherms crosses at a water activity range 0.6–0.8, this phenomenon occurs in food rich in sugars (Simal *et al.*, 2007). For water activities at 0.8 or above, data of equilibrium moisture content at 50 °C are the same or below those at 70 °C. The latter behaviour may be attributed to the effect of temperature on the physicochemical state and the solubility of the sugars (Pezzutti & Crapiste, 1997). The solubility of sugars increases with the temperature converting the crystalline sugar into sugar solution, and thus lowering the water activity. The same behaviour was observed by Simal *et al.* (2007) for pineapple, Kaymak-Ertekin & Gedik (2004) for grapes and apricots and Roman *et al.* (1982) for apples.

Non-linear regression was done by the least square method, utilising GAB, BET, Henderson–Thompson and Oswin models, with the isotherm data obtained experimentally. The adjustment results at different temperatures are shown in Tables 1 and 2 for garlic and apple, respectively.

Analysing Tables 1 and 2, it can be verified that the GAB model presented the best fitting, showed in Figs 1 and 2, with high determination coefficients ($R^2 > 99\%$) and low mean relative error. The fit of a model is good enough practical purposes when $E\%$ is less than 10% (Kaymak-Ertekin & Gedik, 2004). The GAB model has been considered the best fit model for majority of food materials up to $a_w > 0.9$, whereas the BET model gives a good fit to data for $a_w < 0.5$ (Ariahu *et al.*, 2006). According to Lomauro *et al.* (1985), the GAB equation gave the best fit for more than 50% of the fruits, meats and vegetables analysed.

In Tables 1 and 2, it can be verified that the monolayer moisture content decrease with the increase of the temperature. This behaviour is not so clear for garlic (Table 1) although a strong trend is shown. The monolayer moisture content indicates

Table 1 Adjustment parameters of isotherms models of garlic at selected temperatures

	Garlic		
Constants	50 °C	60 °C	70 °C
GAB			
M_m (d.b.)	0.056 ± 0.004	0.052 ± 0.003	0.050 ± 0.002
C_G	7.17 ± 1.77	3.55 ± 0.86	1.75 ± 0.40
K	0.98 ± 0.01	0.98 ± 0.02	0.99 ± 0.01
E (%)	9.76	9.31	9.61
R^2 (%)	99.36	99.29	99.44
BET			
M_m (d.b.)	0.051 ± 0.003	0.048 ± 0.004	0.030 ± 0.006
C_B	10.08 ± 2.95	4.26 ± 1.05	6.06 ± 3.96
E (%)	13.25	16.01	23.77
R^2 (%)	94.93	96.84	83.18
Henderson–Thompson			
a_1	4.305 ± 0.224	4.169 ± 0.171	3.835 ± 0.111
b_1	0.76 ± 0.04	0.703 ± 0.03	0.61 ± 0.02
E (%)	28.53	27.68	26.76
R^2 (%)	97.43	98.15	98.83
Oswin			
a_2	0.095 ± 0.003	0.084 ± 0.002	0.068 ± 0.002
b_2	0.72 ± 0.02	0.77 ± 0.02	0.87 ± 0.02
E (%)	12.45	9.24	17.05
R^2 (%)	99.12	99.24	99.45

Table 2 Adjustment parameters of isotherms models of apple at selected temperatures

Constants	Apple 50 °C	 60 °C	 70 °C
GAB			
M_m (d.b.)	0.168 ± 0.006	0.130 ± 0.002	0.107 ± 0.003
C_G	26.33 ± 7.23	25.39 ± 8.78	15.39 ± 5.48
K	0.98 ± 0.01	0.99 ± 0.02	0.99 ± 0.01
E (%)	9.02	5.77	8.56
R^2 (%)	99.07	99.70	99.53
BET			
M_m (d.b.)	0.146 ± 0.002	0.119 ± 0.005	0.106 ± 0.004
C_B	39.51 ± 5.54	46.11 ± 19.78	21.65 ± 6.35
E (%)	3.92	9.79	9.23
R^2 (%)	99.2	92.62	95.54
Henderson–Thompson			
a_1	1.793 ± 0.04	1.866 ± 0.030	1.703 ± 0.029
b_1	0.84 ± 0.06	0.63 ± 0.04	0.53 ± 0.04
E (%)	89.47	282.05	472.94
R^2 (%)	94.92	95.80	95.54
Oswin			
a_2	0.332 ± 0.014	0.237 ± 0.012	0.211 ± 0.015
b_2	0.67 ± 0.03	0.83 ± 0.03	1.04 ± 0.05
E (%)	24.39	53.64	98.82
R^2 (%)	97.86	98.31	97.51

the quantity of water strongly adsorbed in material sites, and is considered an important measure to know the stable conditions of conservation of food materials. Iglesias & Chirife (1982) studied this phenomenon and verified that it occurs because of the enzymatic reactions and the protein alteration contained in the material.

The values of the two GAB parameters, C_G and K (Tables 1 and 2) have been found to decrease with increasing temperature. Such decreasing trends to reveal that the binding energies associated with the mono and multilayer sorption of water to the garlic and apple decrease with increase in temperature. These trends have been to be quite common for many foods (Chen & Jayas, 1998; Das & Das, 2002). C_G is related to the difference of the chemical potential in the upper layers and in the monolayer, while K is related to this difference in the pure liquid adsorbed and in the upper layers. Thus, the K parameter is, practically without exception, near but less than unity. This fact constitutes a definitive characteristic of the GAB isotherm (Simal *et al.*, 2007).

Figures 3 and 4 present the results of $-\ln(a_w)$ vs. $(1/T)$ at the three analysed temperatures, varying the equilibrium moisture content (M_e) from 5% to 40%, in dry basis (d.b.), for garlic and apple, respectively.

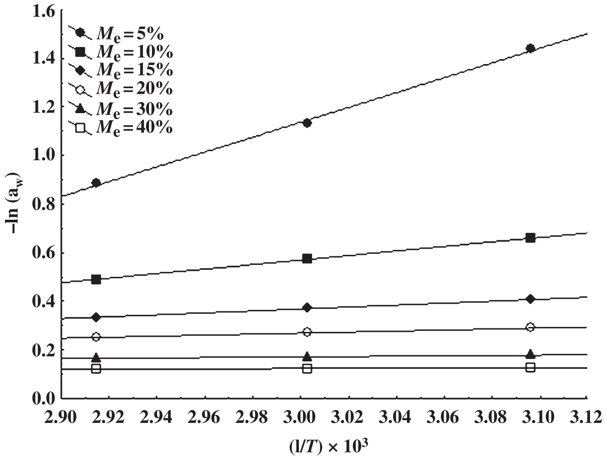

Figure 3 $-\ln(a_w)$ vs. $(1/T)$ curves of garlic, at the analysed temperatures.

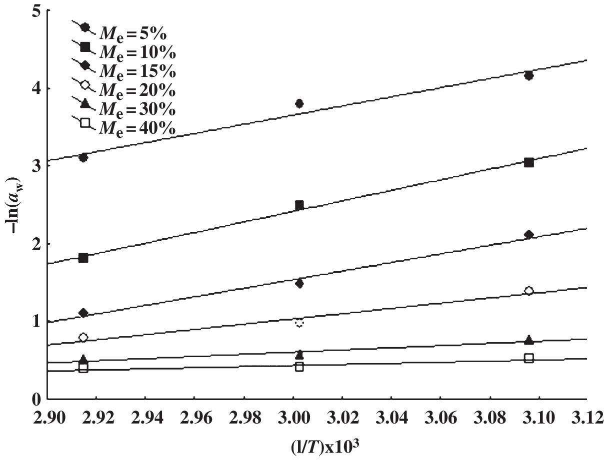

Figure 4 $-\ln(a_w)$ vs. $(1/T)$ curves of apple, at the analysed temperatures.

The values of net isosteric heat of desorption, q_{st}, were calculated from the data of angular coefficients in Figs 3 and 4, according to eqn 10. The values of heat of desorption (Q_{st}), in function of the equilibrium moisture content, calculated by eqn 7, are shown in Fig. 5 for garlic and apple, at 60 °C (drying temperature).

It can be verified through Fig. 5 that the values of heat of desorption for apple were higher than those for garlic. In this figure, we can also verify for the samples that with the increase of equilibrium moisture content, the heat of desorption approaches the heat of vaporisation of pure water at the same temperature. This occurs because as more water is presented in the material the binding energy between water molecules becomes weaker, approaching that of the water molecules in the liquid state. When the material presents low moisture contents, the energy of interaction between water molecules and primary sorption sites in the food solids is greater than the energy that binds the water molecules together in succeeding layers of water.

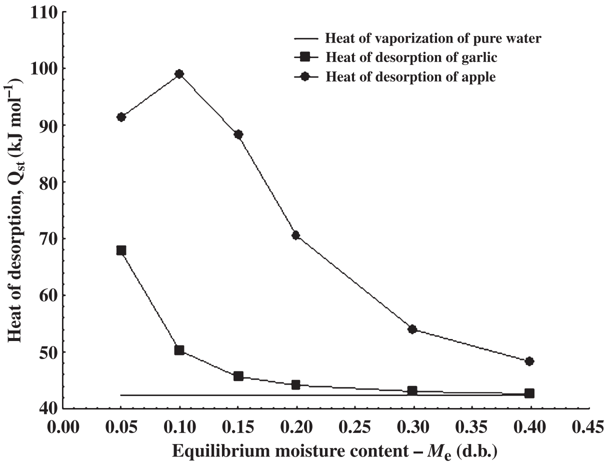

Figure 5 Isosteric heat of desorption of garlic and apple as a function of equilibrium moisture content and heat of vaporisation of pure water, at 60 °C.

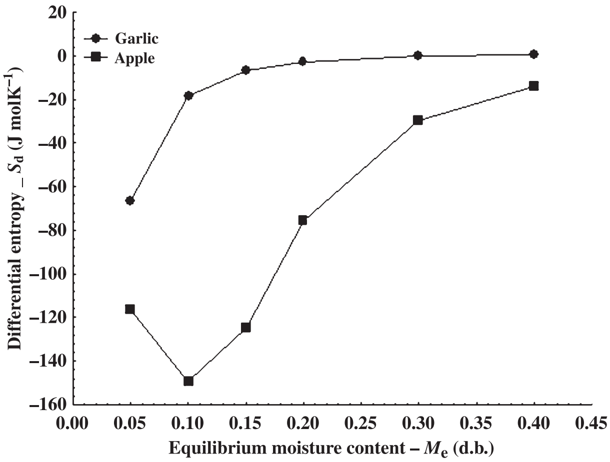

Figure 6 Differential entropy of desorption of garlic and apple as a function of equilibrium moisture content, at 60 °C.

Isosteric heat of desorption of apple increased to a maximum and then decreased with the increase in moisture content according to Fig. 5. The same phenomenon was observed in various studies of food materials, as the case of mulberry (Maskan & Gogus, 1998) and cookies and corn snacks (Palou *et al.*, 1997). Decrease of the heat of desorption below this value of moisture content was qualitatively explained by Maskan & Gogus (1998) in function of the binding energy of water contained in the material sites. The maximum isosteric heats of apple were obtained in the moisture content of 10% d.b. and were 98.9 kJ mol^{-1}. The maximum enthalpy value indicates the covering of the strongest binding sites and the greatest water–solid interaction. The covering of less favourable locations and the formation of multilayers then follow, as shown by the decrease in enthalpy with increasing moisture content.

Differential entropy values (S_d) were calculated from the y-intercept of these straight lines, determined through linear regression for the six values of equilibrium moisture content, according to eqn 10. Figure 6 shows the differential entropy for garlic and apple as a function of moisture content, at 60 °C. In Fig. 6, the values of differential entropy of apple were lower than those of garlic. These values increase with the increase in moisture content, but remain negative values. This is an indication of thermodynamic compensation between the heat and entropy of moisture sorption by the materials (garlic and apple). At lower moisture content values, the water molecules are tightly bound on the sorbent surfaces and therefore have low degree of freedom resulting in low entropy of sorption. At higher moisture contents, the water molecules are sorbed on multilayer on the top of the tightly bound first layer. The multilayer water molecules have greater degree of freedom and hence higher entropy of sorption. Moisture adsorption is essentially exothermic while desorption is mainly endothermic (Ariahu *et al.*, 2006).

Analysing Fig. 6 can be verified that the differential entropy of apple was lower at lower moisture content, but it then increased rapidly with increase in moisture content in moisture of 10% [dry basis (d.b.)]. Below a moisture content of 10%, the differential entropy of apple increased sharply with decrease in moisture content.

Table 3 presents the water surface area of garlic and apple between 50 and 70 °C. These values were estimated using eqn 11 and the monolayer moisture contents were obtained by GAB model. The results presented in Table 3 indicate that the total surface area available for desorption decreased with increasing temperature. The values of surface area for garlic were lower than those for apple as the monolayer moisture values for garlic were lower in comparison with apple. The large surface area of many foodstuffs is due to the existence of an intrinsic microspore structure in these materials (Calzetta Resio *et al.*, 2000). Tolaba *et al.* (2004) for quinoa grains, reported the surface area values of 303.45, 297.85 and 206.5 m^2 g^{-1} for adsorption and 349.65, 303.1 and 200.55m^2 g^{-1} for

Table 3 Water surface area (S_0) of garlic and apple, at different temperatures

T (°C)	S_0 garlic (m^2 g^{-1} solid)	S_0 Apple (m^2 g^{-1} solid)
50	315	588
60	301	455
70	196	374.5

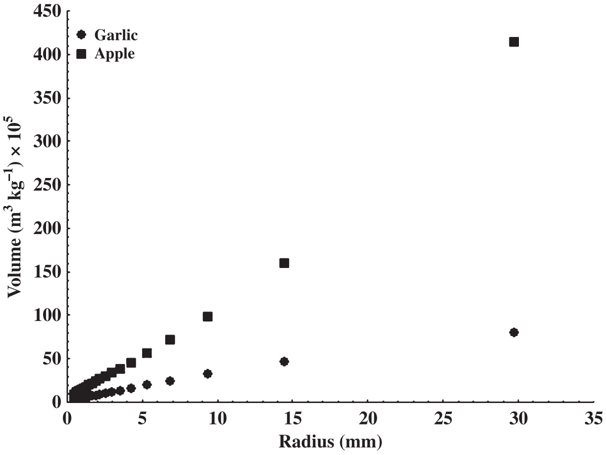

Figure 7 Integral curve of liquid volume in the pores vs. its radius of garlic and apple, at 60 °C.

desorption, for the temperatures of 20, 30 and 40 °C, respectively.

Figure 7 gives the relation of the pore volume vs. its radius. It can be verified in Fig. 7 that the pores sizes varied from 0.5 to 30 nm during desorption of garlic and apple depending on moisture content. At higher moisture levels, the pores sizes were larger. According to these values, garlic and apple pores can be classified as microspores and mesopores according to IUPAC (International Union of Pure & Applied Chemistry) classification (Lastoskie *et al.*, 1993).

Conclusion

The GAB model presented the best fitting the equilibrium isotherms data of garlic and apple, with high determination coefficient values ($R^2 > 99\%$) and low mean relative error values ($E\% < 10\%$). The monolayer moisture content values (M_{m}) for garlic and apple, at the analysed temperatures, were estimated in the range 5.0–5.6% and 10.7–16.8%, in d.b., respectively.

The heat of desorption values for apple were higher than those for garlic calculated through the Clausius–Clapeyron equation. The Gibbs equation was used to calculate the differential entropy. The values of differential entropy for garlic were found to be greater than those for apple, and the differential entropy for apple decrease with decreasing moisture content until reach a minimum value (-150 J mol^{-1} K^{-1}), and then increase sharply.

The water surface area values decreased with increasing of temperature. The pores of garlic and apple were determined with the Kelvin and the Halsey equations, and they were found to be microspores and mesopores according to IUPAC and the pores sizes varied from 0.5 to 30 nm.

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