Equilibrium Moisture Content and Heat of Desorption of Garlic

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Abstract

Desorption isotherms for 1 mm thick garlic slices were determined by a static gravimetric method at temperatures between 5 and 45ºC, in the relative humidity range from 11 to 98%. The experimental desorption data obtained in this study was fitted to BET and GAB equations to predict the desorption behaviour of garlic. It was found that the GAB model was the most satisfactory model for representation of the sorption data. Monolayer moisture contents (X_m) were calculated from the BET and GAB equations. The X_m values of both models decreased with increasing temperature. The net isosteric heat of desorption, estimated using the Clausis-Clapeyron equation, range from 4.40×10^2 kJ/kg at a moisture content of 0.05 kg of water/kg dry mass to 99.2 kJ/kg at 0.3 kg of water/kg dry mass.

The results obtained in this study, are now being used in the development of a drying unit for garlic, by a suitable technique.

1 Introduction

Garlic (*Allium sativum* L.) has been cultivated for centuries all over the world on account of its culinary and medicinal properties. Clinical trials have shown that garlic has important health benefits. The most encouraging results have occurred in the area of cholesterol reduction (Reuter et al., 1996). The compound responsible for these benefits is allicin, which gives garlic's characteristic flavour and odour. More recently, it has found uses as a raw material in the pharmaceutical industry and, in its dried form, as an ingredient of precooked and instant convenience foods, which has led to a sharp increase in the demand for dried garlic.

Moisture sorption isotherms describe the relationship between the equilibrium moisture content and the water activity at constant temperatures and pressures. For food materials these isotherms give information about the sorption mechanism and the interaction of food biopolymers with water. The moisture sorption isotherms are extremely important in modelling the drying process, in design and optimisation of drying equipment, in predicting shelf-life stability, in calculating moisture changes which may occur during storage and in selecting appropriate packaging material (Gal, 1987). Numerous mathematical models have been reported in literature for describing water sorption isotherms of food materials. They vary a lot in terms of origin (empirical, semi-empirical or theoretical) and range of applicability (a_w limit and type of food). Mathematical models are of special interest in many aspects of food preservation by dehydration.

The net isosteric heat of sorption can be used to estimate the energy requirements for the dehydration process. The level of material moisture content at which the net isosteric heat of sorption approaches the latent of vaporization of water is often taken as an indication of the amount of "bound water" existing in the food (Kiranoudis et al., 1993). The heat of vaporization of sorbed water may increase to values well above the vaporisation of pure water as food is dehydrated to low moisture levels.

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There is very little published work on the desorption isotherms and drying kinetics of garlic. Pezzutti and Crapiste (1996) have investigated drying characteristics of garlic including moisture sorption equilibrium, drying kinetics and pungency losses. Vásquez et al. (1999) have determined desorption isotherms at temperatures between 25 and 45ºC and the drying kinetics of garlic slices, varying slice thickness and the temperature and air flow rate in the drying chamber.

The objective of the present study was to determine the effect of temperature on the moisture desorption isotherms of garlic in the temperature range 5-45ºC, analyse two sorption isotherm equations available in the literature, find the suitable model corresponding to the isotherms of garlic, to evaluate and compare monolayer moisture content (X_m) obtained with BET and GAB equations and to determine the net isosteric heat of desorption of garlic.

2 Experimental Section

Preparation of the substrate

Fresh heads of garlic were purchased from Badajoz, Spain market. Table 1 shows a typical composition of garlic. The garlic bulbs were stored in a cold chamber maintained at a temperature of 4ºC and 70% relative humidity. The initial moisture content of the garlic was determined at 103ºC in the Sartorius moisture balance (Figure 1, A) and range from 1.55-1.85 kg of water/kg dry mass, wich compare with the typical composition of garlic, Table 1. Before the experiments the garlic samples were pre-treated for 24 hours at room temperature (5, 15, 25, 35 and 45ºC) to acquire 100% of relative humidity. The garlic heads were separated into cloves, peeled and then cut into slices of 1 mm of thickness.

Table 1. Average percentage of composition of garlic.

Component	%
Water	63
Minerals	17
Vitamin	14
Proteins	3
Carbohydrates	2
Calories	1

Procedure for Desorption Isotherms Determination

Novasina AW SPRINT (Figure 1, C) with saturated salts solutions was used for the determination of desorption isotherms for 1 mm thick garlic slices at temperatures between 5 and 45ºC, in the relative humidity range from 11 to 98%. To inhibit microbial growth a small quantity of thymol was also placed in the recipient for water activity higher than 0.7. The garlic samples were weighed at smaller periods (initial phase) and then at every 24 hours (latter phase) in the Denver Instrument balance (Figure 1, B), until their mass varied ≤ 0.03% between weightings.

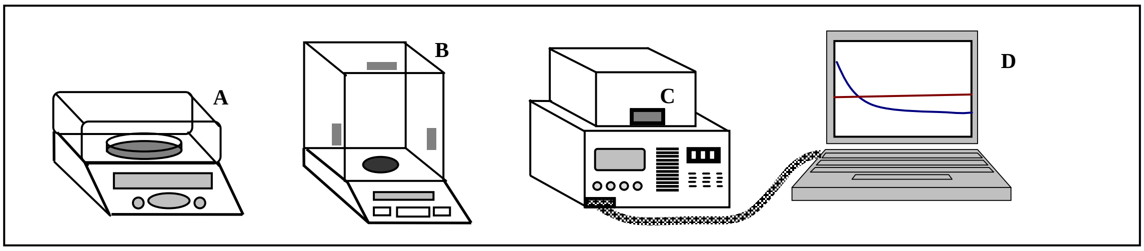

Figure 1. Schematic diagram of apparatus used in the determination of desorption isotherms: (A) Sartorius MA45 (moisture balance); (B) Denver Instrument (analytical balance); (C) Novasina AW SRINT (water activity measuring) and (D) Computer for data recorded with the NOVALOG32 PC-software.

At the end of the experiment the garlic slice and the saturated salt solution are in equilibrium, and the final mass were used to determine the moisture content at the corresponding water activity. This moisture content was subsequently adjusted by dividing it by the dry mass, which was determined using the Sartorius MA45 moisture balance (Figure 1, A) (at 103ºC) after the final equilibrium had been reached.

3 Theory

Modelling of Desorption Isotherms

Models of sorption isotherms are of great utility in the design of drying process, and often afford parameters that are characteristic of the stability of the stored foodstuff and thus can be used to predict its shelf life. The BET (Brunauer-Emmett-Teller (1938)) and the GAB (Guggenheim (1966), Anderson (1946) and De Boer(1953)) which are easily linearized are widely used for estimating monolayer moisture contents and heats of sorption. However, the GAB model adjusts more successfully in a wide water activity range and was recommended by European project group COST 90 on physical properties of foods (Bizot, 1983). When k=1, GAB model reverts to the BET model. The BET and GAB models are described mathematically by the following equations:

$$X_e = \frac{X_m C a_w}{(1-a_w)(1-a_w+Ca_w)} \text{ (BET equation)} \tag{1}$$

$$X_e = \frac{X_m C k a_w}{(1-ka_w)(1-ka_w+Cka_w)} \text{ (GAB equation)} \tag{2}$$

where X_e is the equilibrium moisture content (kg of water/kg dry mass), a_w is the water activity, X_m is the monolayer moisture (kg of water/kg dry mass) content and C and k are the fitting constants of the BET and GAB model.

Calculation of Model Parameters

For the calculation of model parameters from moisture desorption data, the BET ($k = 1$) and GAB ($k \neq 1$) equations (Eq. 1 and 2) were transformed into the following linear relation:

$$\frac{ka_w}{(1-ka_w)X_e} = a + bka_w \tag{3}$$

where

$$a = \frac{1}{X_m C} \tag{4}$$

and

$$b = \frac{C-1}{X_m C} \tag{5}$$

The goodness of a fit relatively to experimental data was evaluated through a mean relative percentage deviation (P) between the predicted (X_{pi}) and experimental (X_i) moisture contents defined as:

$$P(\%) = \frac{100}{n}\sum_{i=1}^{n}\frac{|X_i - X_{pi}|}{X_i} \tag{6}$$

Net Isosteric Heat of Desorption

The net isosteric heat of desorption, is defined as the total heat of sorption of water from the material minus the heat of vaporization of liquid water. The commonly used method to calculate the net isosteric heat of desorption is from the Clausius-Clapeyron equation:

$$\left[\frac{d\ln(a_W)}{d(1/T)}\right]_{X_e=const} = -\frac{Q_n^{st}}{R} \tag{7}$$

where Q_n^{st} is the net isosteric heat of desorption (kJ/kg), a_w is the water activity (decimal), X_e is the equilibrium moisture content (kg of water/kg dry mass), R is the gas constant (0.4618 kJ/kgK) e T is the absolute temperature (K). The net isosteric heat of desorption (Q_n^{st}) can be calculated by plotting the desorption isotherms as ln(a_w), at a specific moisture content *versus 1/T* and measuring the slope which equals the Q_n^{st} / R. The application of this method requires the measurement of desorption isotherms at least three temperatures.

4 Results and Discussion

The moisture desorption isotherms obtained from desorption data of the garlic samples at 5, 15, 25, 35 and 45ºC are show in Figure 2. According to Brunauer´s (Brunauer, 1945) classification, all of the isotherms determined were of type III. A type III isotherm appears when the binding energy of the first layer is lower than the binding energy between water molecules (Leung, 1986). The equilibrium moisture content increased at the same water activity as the temperature decrease (Figure 2). However the diference is not significative. The reason may be because water molecules at lower temperatures have a lower kinetic energy which is not enough to overcome the corresponding sorption energy (Lagoudaki et al., 1993).

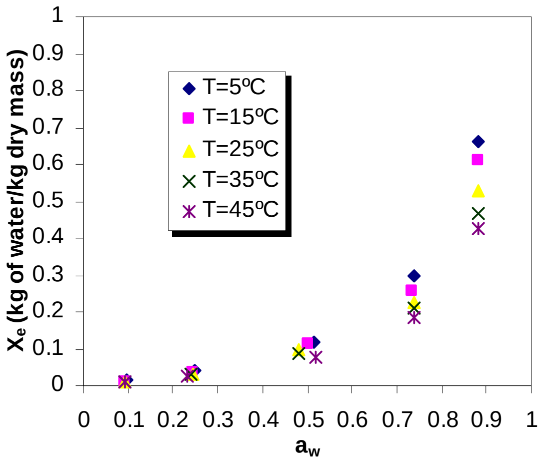

Figure 2. Moisture desorption isotherms of garlic at 5, 15, 25, 35 and 45ºC.

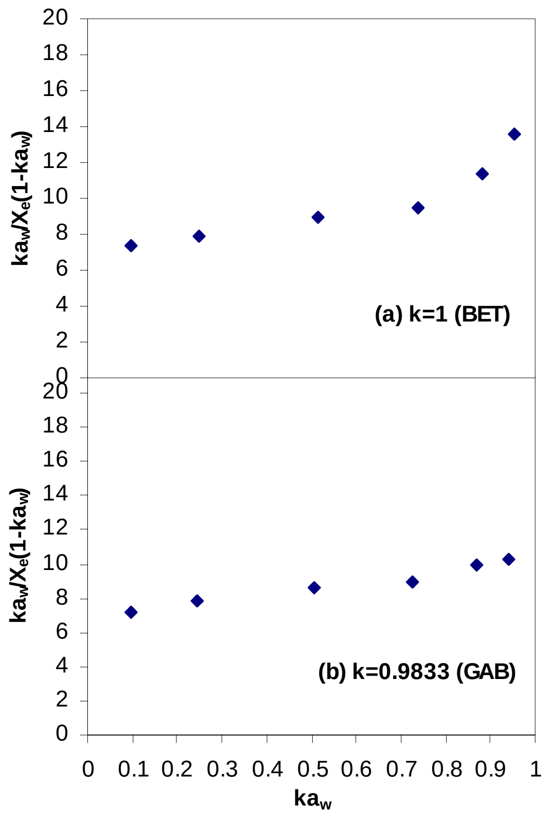

Figure 3. Plot of $ka_w/X_e(1\text{-}ka_w)$ *vs* ka_w for desorption of garlic at 5ºC: (a) $k=1$ (BET isotherm); (b) $k=0.9833$ (GAB isotherm).

Figure 3 shows a plot of $ka_w/X_e(1\text{-}ka_w)$ *versus* ka_w for the analysis of the most suitable model to describe the isothermal water desorption in garlic, Figure 3 (a) BET isotherm and Figure 3 (b) GAB isotherm. Figure 3 (b), clearly shows that the GAB model is the best to fitting desorption data. The parameters of the GAB and BET model obtained at the temperatures studied are in Table 2 together with mean relative percentage deviation, which also indicate that the GAB model is the best to fit experimental data.

The monolayer moisture content (X_m) is an important parameter in food storage and deterioration of dry products and can be obtained by the BET and GAB models (Chung & Pfost, 1967). Table 2 shows that the monolayer moisture contents of garlic decrease with increasing temperature. The X_m values range from 0.0988 to 0.0682 kg of water/kg dry mass at temperatures between 5 and 45ºC, respectively for the GAB model and range from 0.0806 to 0.0579 kg of water/kg dry mass at temperatures between 5 and 45ºC, respectively for the BET model. These values of X_m correspond to a water activity of around 0.5, which is comparable to the values obtained by some authors (Pezzutti and Capiste, 1996 and Vásquez et al., 1999) for garlic cultivar in Argentine and Spain. The X_m values obtained by the GAB model were higher than those obtained by the BET model. Similar results were also obtained by other investigators (Palou et al., 1997; Wang & Brennan, 1991).

Table 2. Fitting parameters of BET and GAB models for the desorption isotherms of garlic at 5, 15, 25, 35 and 45ºC.

	T(ºC)	X_m (kg of water/kg dry mass)	*C*	*k*	*P(%)*
	5	0.0806	1.9815	1	6.77
	15	0.0753	1.8903	1	8.76
BET	25	0.0669	1.9368	1	8.13
	35	0.0562	2.2376	1	11.61
	45	0.0579	1.4909	1	11.61
	5	0.0988	1.4613	0.9833	1.37
	15	0.0888	1.5034	0.9865	3.51
GAB	25	0.0763	1.5994	0.9892	4.08
	35	0.0723	1.5261	0.9792	3.96
	45	0.0682	1.2385	0.9758	0.65

The results arising from this work show that the GAB model could be used as an adequate desorption model for desorption data of garlic.

The net isosteric heat of desorption (Q_n^{st}) values were calculated from the slope of the plot between the values of $\ln(a_w)$ and *1/T* at constant moisture content, according to Equation 7, as are shown in Figure 4.

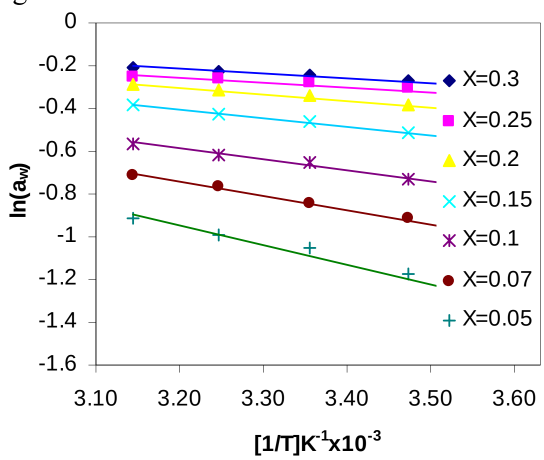

Figure 4. $\ln(a_w)$ vs *1/T* graphs for calculating the heat of desorption of garlic.

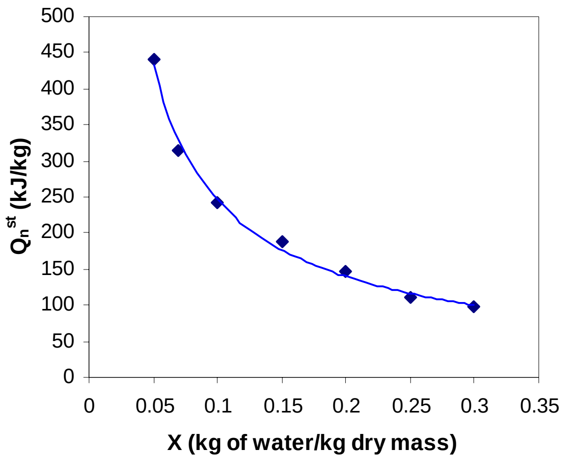

Figure 5. Net Isosteric heat of desorption of garlic (Q_n^{st}) for different moisture contents.

The net isosteric heat of desorption (Q_n^{st}) values were calculated from the slope of the plot between the values of $\ln(a_w)$ and *1/T* at constant moisture content, according to Equation 7, as are shown in Figure 4. The net isosteric heat of desorption of garlic decrease with increasing moisture content as shown in Figure 5. The (Q_n^{st}) values range from 4.40×10^2 kJ/kg at 0.05 kg of water/kg dry mass to 99.2 kJ/kg at 0.3 kg of water/kg dry mass. Above a moisture content of 0.3 kg of water/kg dry mass the net isosteric heat is constant and low (indicating the presence of free water) and below this value the net isosteric heat increases appreciably by the existence of bound water that is strongly bound to the product. The net isosteric heat of desorption of water in garlic can be expressed mathematically as a potency function of moisture content:

$$Q_n^{st} = 37.567 X^{-0.8154} \qquad (r = 0.994) \qquad (8)$$

5 Conclusions

The equilibrium moisture content of garlic has been determined by the static gravimetric method at five temperatures. Among the two sorption models chosen to fit the desorption curves, the GAB model gave the best results for the desorption isotherms of garlic. The net isosteric heat of desorption of garlic decreses with an increasing in moisture content and can be representably by a potency function. The values obtained were not very high and only must be considered at low moisture content (below 0.3 kg of water/kg dry mass).

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