Moisture Adsorption Characteristics of Ginger (*Zingiber officinale*) Powders

J. S. Alakali[1] and A. A. Satimehin[2]

[1]Department of Food Science and Technology, University of Agriculture, Makurdi, Nigeria
[2]Department of Agricultural and Environmental Engineering, University of Agriculture, Makurdi, Nigeria

adeadesat@yahoo.co.uk (A. A. Satimehin)

ABSTRACT

The adsorption equilibrium moisture content of the powders of peeled ginger (PGP) and unpeeled ginger (UGP) at 20, 30, 40 and 50 °C were investigated using static gravimetric method. The data were fitted to various sorption models. The thermodynamics of water vapour adsorption of the powders was also investigated at moisture contents in the range of 8 to 20 g H_2O/100 g solid. Both powders exhibited the type II isotherms. The equilibrium moisture content of the powder decreased with increasing temperature and increased with water activity. The monolayer moisture content also decreased with an increase in temperature. The powder of peeled ginger was less hygroscopic than that of unpeeled ginger and is therefore more shelf-stable. The GAB, Henderson and Oswin equations accurately fitted experimental sorption data (RMS < 10 %); however, the GAB model gave the best fit. The net isosteric heats (ΔH_{st}) of sorption generally decreased with increasing moisture content. The ΔH_{st} of UGP was generally higher than that of PGP. The isosteric heat of the first molecule (ΔH_o) of UGP was also higher (72.042 kJ/mol) than that of the PGP (59.695 kJ/mol). On the other hand, the characteristic moisture content (M_{ch}) of UGP was lower (4.058 g H_2O/100g solid) than its equivalent for PGP (4.155 g H_2O/100 g solid). The values of ΔH_o and M_{ch} indicated the relative low moisture affinity of UGP compared to PGP. The enthalpies of sorption for PGP were lower than UGP. Conversely, the entropy of sorption of UGP was higher (6.233 to 158.180 J/mol-K) than that of PGP (2.496 to 125.721 J/mol-K).

Key words: Ginger powders, moisture adsorption, isotherms, isosteric heat, entropy.

1. INTRODUCTION

Ginger (*Zingiber officinale)* is a spice believed to be indigenous to South East Asia, from where it has spread to other tropical regions of the world (Wiley, 1974). India accounts for about 50% of world ginger supply. Other major producers include Nigeria, Sierra Leone, Jamaica, China and Haiti (Paulose, 1973; Meadow, 1988).

Ginger has proximate composition of 3-6 % fatty oil, 9 % protein, 60-70 % carbohydrate, 3-8 % fiber, 8 % ash, 12 % water and 2-3 % volatile oil. The volatile oil contains oleoresin, which is responsible for the pungency in ginger. The aromatic and pungent characteristics of ginger make it desirable in the culinary art. The economic importance of ginger centers on its use in the preparation of medicines. The extracts of ginger have multiple pharmacological effects, some of which Guyer (2003) outlined to include inhibition of prostaglandin, thromboxane and

leukotrienes synthesis. Ginger extracts are important in the inhibition of cold and, platelet aggregation. They are also important for their cardiotonic effects and gastro-intestinal actions. Ginger extracts have thermogenic and antibiotic activities and are important as digestive stimulants (Guyer, 2003). Ginger is used in food, beverages and confectionary (Rodriquez, 1971). It is also used industrially in the manufacture of items such as ginger ale, ginger beer, ginger wine, ginger bread, ginger essence, ginger chocolate pastries and biscuits.

Ginger is marketed internationally in the form of three primary products: fresh (i.e. in its green state), preserved and dry ginger. Fresh ginger is consumed as vegetable, preserved ginger is prepared from the immature rhizome while the more pungent and aromatic spices are prepared by harvesting and drying the mature rhizome (peeled or unpeeled). The demand for dry ginger in the local and international market is becoming greater. This implies that more attention should be given to improved drying and storage of ginger to enhance its economic value and increase its shelf life. Dry ginger, like other agricultural products, is hygroscopic and is hence affected by environmental conditions such as temperature and relative humidity. There is therefore the need to study the moisture adsorption characteristic of ginger. Moisture adsorption characteristics of ginger will serve as useful information for the prediction of shelf life and for effective packaging. At specified temperatures, moisture sorption isotherms characterize the water binding of a material at equilibrium and at different water activities. They therefore make it possible to predict the effect of changes in temperature and pressure on the amount of water absorbed or desorbed by materials (Fortes and Okos, 1981; Gevaudan *et al.*, 1990).

The primary objective was to investigate the moisture adsorption characteristics of ginger powders. The specific objectives were to compare the accuracy of three moisture adsorption model equations to describe adsorption data for ginger powders and to determine the thermodynamic properties namely, isosteric heat, enthalpy and entropy of moisture adsorption of ginger powders.

2. THEORETICAL BACKGROUND

Water is held in hygroscopic materials by physical and chemical forces (Cenkowski *et al.*, 1992) and the mechanism of moisture binding is affected by the sorption characteristics of the material. The relationship between equilibrium moisture content (M) and water activity (a_w) at specified temperature is expressed as sorption isotherms. Moisture sorption isotherms provide valuable information on the thermodynamics of moisture sorption (Gevaudan *et al.*, 1990), and serve as useful tool for determining the interaction of water and food substances.

2.1 Moisture Sorption Models

Several mathematical models have been developed to describe the sorption isotherms of foods (Palou *et al.*, 1997; Diosady *et al.*, 1996; Gevaudan *et al.*, 1990; Van den Berg, 1985; Bizot, 1983). The Guggenheim-Anderson-de Boer (GAB) equation (Van den Berg, 1985; Teoh *et al.*, 2001) is a semi-theoretical multi-molecular, localized homogeneous adsorption model. It has been recommended by the European project Group COST '90 on physical properties of foods

(Wolf et al., 1985). GAB model has been reported to give the best fit for many food materials (Menkov et al., 2005; Lomauro et al., 1985; Bizot, 1983). The model is:

$$\frac{M}{M_0} = \frac{GKa_w}{\left(1 - Ka_w\right)\left(1 - Ka_w + GKa_w\right)}$$ (1)

where M = equilibrium moisture content, M_o = monolayer moisture content, a_w = water activity. G and K = constants related to the energies of interaction between the first and distant sorbed molecules, respectively, at individual sorption sites. Bizot (1983) transformed equation (1) into a quadratic equation as follows.

$a_w /M = Aa_w^2 + Ba_w + C$ (2)

With

$A = K/M_o [(1/G) - 1]$ (3)

$B = 1/M_o[1 - (2/G)]$ (4)

$C = 1/M_oGK$ (5)

Equation (2) may be re-arranged to yield the following equation:

$M = a_w /(Aa_w^2 + Ba_w + C)$ (6)

From equations (3) - (6):

$M_o = [1/B^2 + 4AC]^2$ (7)

Henderson (1952), developed a sorption isotherm model describing the temperature effect as:

$ln(1 - a_w) = ATM^B$ (8)

where A and B = constants, T = Temperature (° C)

Oswin (1946) developed an empirical sorption isotherm model equation using a mathematical expression. The Oswin equation is:

$M = A[a_w /(1 - a_w)]^B$ (9)

The Oswin model has been found as a good fit model for sorption of various foods (Lomauro et al., 1985).

2.2 Isosteric Heat of Sorption

Important thermodynamic parameters derived from moisture sorption isotherms are the net isosteric heat of sorption, the enthalpy and entropy of sorption. The net isosteric heat of sorption provides useful information on the heat and free energy changes during moisture sorption processes in foods (Sopade and Ajisegiri, 1994). Several researchers have reported the relationship between equilibrium moisture content data and isosteric heat of sorption for many food substances. Notable among them are Aguerre et al. (1988) for some cereals and grains, Tsami et al. (1990) for dried foods, Wang and Brennan (1991) for potatoes, Sopade and Ajisegiri (1994) for maize and sorghum. Recently, Telis-Romero et al. (2005) applied the isokinetic theory to water sorption in mango pulp and concluded that that the process was enthalpy-controlled.

Clausius-Clapeyron equation, because of its theoretical basis, is often used in determining the total heat of sorption (h^*_{fg}) of agricultural products (Iglesias and Chirife, 1976; Ezeike, 1988; Wang and Brennan, 1991; Cenkowski et al., 1992; Telis-Romero et al., 2005). At a constant amount of sorbed water, the equation is expressed as follows:

$$\left.\frac{d\ln P}{dT}\right|_{na} = \frac{h_{fg}^*}{R_o T^2} \tag{10}$$

where P is the water vapour pressure of the product at the specified temperature, T, and R_o is the universal gas constant.

For pure water, equation (10) becomes

$$\frac{d\ln P_o}{dT} = \frac{h_{fg}}{R_o T^2} \tag{11}$$

where P_o is the saturation water vapour pressure at the temperature, T, and h_{fg} is the heat of vaporization of pure water.

Subtracting equation (11) from equation (10) yields

$$\left.\frac{d\ln(P/P_o)}{dT}\right|_{na} = \left.\frac{d\ln a_w}{dT}\right|_{na} = \frac{\Delta H_{st}}{R_o T^2} \tag{12}$$

where ΔH_{st} is the net isosteric heat of sorption and is equal in value to h_{fg}^* - h_{fg}.

Integrating equation (12) yields

$$\ln a_w = \left(\frac{-\Delta H_{st}}{R_o}\right)\frac{1}{T} + C_{st} \tag{13}$$

where C_{st} is the constant of integration.

A mathematical model which expresses the total heat of sorption as function of moisture was developed by Gallagher (1951) and is commonly cited in the literature (Ezeike, 1988; Cenkowski *et al.*, 1992; Satimehin and Ezeike, 2003). The equation is given as follows:

$$h_{fg}^* = h_{fg}\left[1 + a\exp(bM)\right] \tag{14}$$

Rearranging equation (14) leads to the following equation proposed by Tsami *et al.* (1990):

$$\Delta H_{st} = \Delta H_0 \exp\left[-\frac{M}{M_{ch}}\right] \tag{15}$$

where ΔH_o is the isosteric heat of sorption of the first molecule of water in the food (kJ/mol). M_{ch} is a characteristic moisture content (g H_2O/100 g solid) of the food material; it is the moisture content at which the net isosteric heat of desorption has been reduced by 63% (Kiranoudis *et al.*, 1993).

2.3 Enthalpy and Entropy of Sorption

The GAB thermodynamic constants G and K are related to moisture sorption enthalpy of the monolayer and multilayer (Diosady *et al.*, 1996; Rizvi, 1995) by equations (16) and (17), respectively.

$$G = G'\exp\frac{\Delta H_G}{R_0 T} \tag{16}$$

$$K = K'\exp\frac{\Delta H_K}{R_0 T} \tag{17}$$

where $\Delta H_G = H_m - H_n$ and $\Delta H_K = h_{fg} - H_{n.}$

G' and K' are entropic accommodation factors, H_m is sorption enthalpy of monolayer, H_n is sorption enthalpy of multilayer.

The entropy of sorption may be obtained from the Gibbs free energy of sorption and related to temperature as follows (Ariahu *et al.*, 2006; Rizvi, 1995).

$$\Delta G^o = \Delta H_{st} - T\Delta S^o \qquad (18)$$

where ΔG^o is Gibbs free energy (kJ/mol) and ΔS^o is isosteric entropy of sorption (kJ/mol K). According to Rizvi (1995), Gibbs free energy is related to water activity as follows:

$$\Delta G^o = R_0 T \ln(a_w) \qquad (19)$$

From equations (18) and (19), it follows that:

$$\ln(a_w) = \frac{-\Delta S^0}{R_0} + \frac{\Delta H_{st}}{R_0 T} \qquad (20)$$

The ΔS^o values were determined from the intercept coefficient derived from least squares regression of the plot of $\ln(a_w)$ versus $1/T$ at constant moisture content.

3. MATERIALS AND METHODS

3.1 Materials

About 6 kg of fresh yellow ginger (*Zingiber officinale*) were purchased from a local market in Makurdi, Nigeria. The ginger was divided into two lots. Lot I was carefully peeled with a stainless steel knife and sliced into 2 mm thick rectangular flakes. Lot II was also sliced into flakes of the same dimensions as in Lot I, but was not peeled. Both samples were dried in an air convection electric oven (Genlab model T12H, England) at 85 °C for 24 hours to constant weight. The dry samples were milled using a bench-top hammer mill (Brook Compton Series 2000, England) and sieved through a 500 µm mesh screen. The resulting powder from Lot I, was designated peeled ginger powder (PGP) and from Lot II as unpeeled ginger powder (UGP). The powders were further dried in desiccators over concentrated sulphuric acid for seven days to remove residual moisture. The samples were then packed in 10 g inside polythene bags and sealed with an impulse sealer (Model ME-200HN, MEC Mercier Corporation, Taiwan).

Various concentrations of sulphuric acid were used in creating relative humidity ranging from 3.5 to 93.9 % at 20, 30, 40, and 50 °C. Relative humidity data of the sulphuric acid solutions at the stated temperatures were obtained from literature (Weast and Astle, 1989).

Moisture adsorption was determined gravimetrically as described by Mok and Hettiarachchy (1990). A 2×4×9 randomized factorial design consisting of two samples (PGP and UGP), four temperatures (10, 20, 30 and 40 °C) and nine water activities ranging from 0.035 to 0.939 was used. Samples weighing 0.5 g were placed in sample holders, which were in turn suspended over stainless steel gauze in the constant relative humidity environments and allowed to equilibrate at the selected temperatures in a Gallenkamp incubator (Model INF 600.010 R, Sanyo, UK). The temperatures were monitored and controlled within ±1 °C. The samples were weighed at 48

hours intervals until three successive readings were each less than 0.5 % of the previous one. All tests were replicated three times.

3.2 Analysis of Moisture Adsorption Data

Equilibrium moisture content versus water activity data were plotted and analyzed using the GAB, Henderson and Oswin models. The parameters of the models were calculated by direct non-linear regression analysis using SPSS 6.0 (SPSS Inc., USA). The accuracy of the models was compared by calculating their percent root mean square of error (%RMS) prescribed by Mok and Hittiarachchy (1990) as follows:

$$\%RMS = \sqrt{\frac{\sum \left[\frac{M_i - M_p}{M_i}\right]^2}{N}} * 100\% \qquad (21)$$

where M_i and M_p are experimental and predicted moisture values respectively, N = number of experimental data.

Equation (13) was fitted to the moisture adsorption data. A least-squares regression analysis was performed to obtain the slope ($-\Delta H_{st}/R_o$) of the straight line representing $\ln(a_w)$ versus $1/T$. Equation (15) was fitted to the data for ΔH_{st} and moisture content (M) by least square non-linear regression to obtain values of ΔH_o and M_{ch}. The values of entropy, ΔS^o, were obtained from equation (20) by plotting $\ln(a_w)$ versus $1/T$ at constant moisture content.

4. RESULTS AND DISCUSSION

4.1 Moisture Sorption Isotherms

Moisture sorption isotherms for the peeled (PGP) and unpeeled (UGP) ginger samples are presented in figures 1 and 2, respectively. The isotherms exhibited S-shapes described as type II in the isotherms classification (Iglesias and Chirife, 1982). According to Bolin (1980) and Bandyopadhyay *et al.* (1987), the type II isotherms are typical of foods high in carbohydrates. Hence this shape of the isotherms was expected of ginger powder because of their high carbohydrate content of 60-70 %.
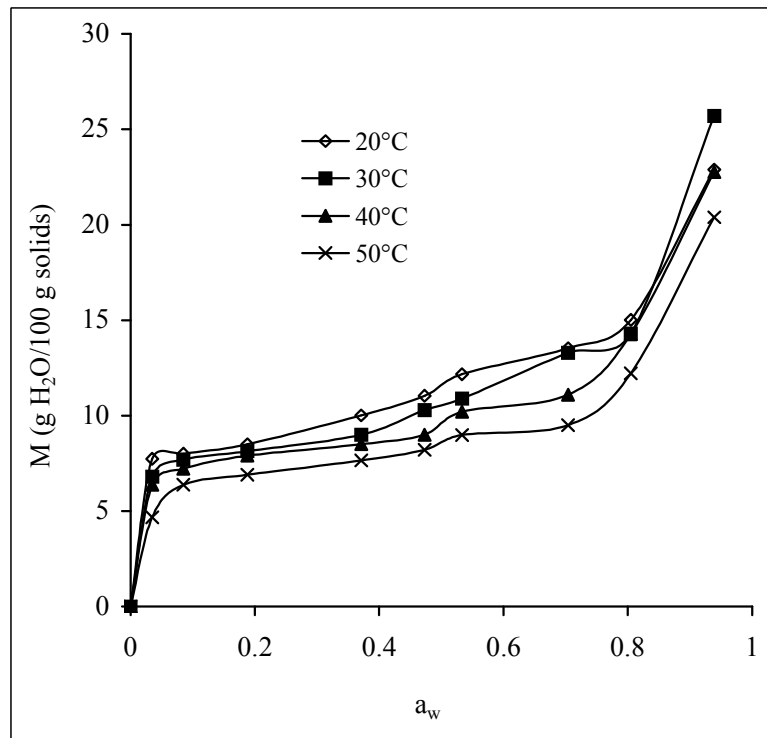
Figure 1. Moisture adsorption isotherms of PGP
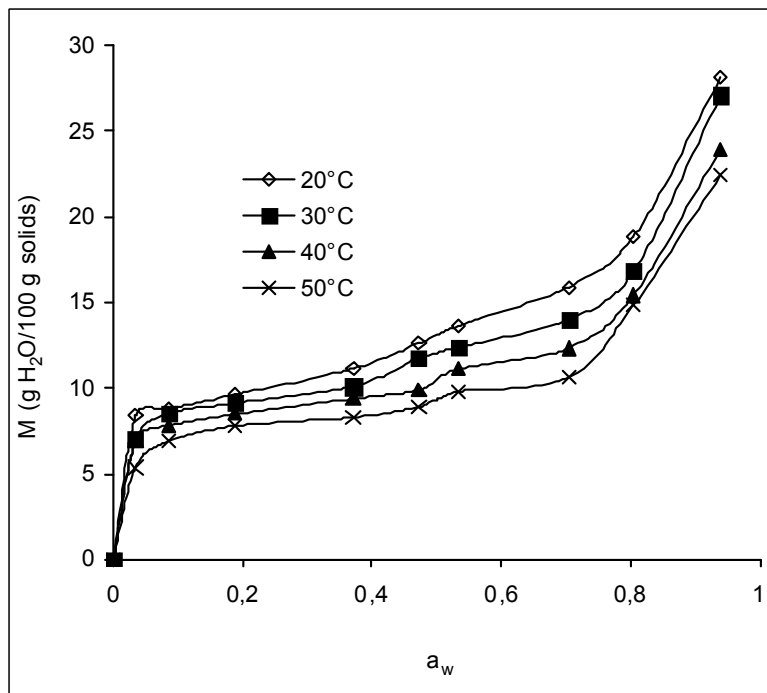
Figure 2. Moisture adsorption isotherms of UGP

The equilibrium moisture content (EMC) of the samples increased as the water activity increased at constant temperature. Slopes of the isotherms were gentle at $a_w < 0.55$ where relatively low moisture was absorbed for a high increase in a_w. Above this level, however, high amount of water was absorbed for a small rise in a_w. For a considerable increase within the low water activity region ($0.035 \leq a_w \leq 0.533$) at 20 °C, there was only a small increase in EMC from 0.64 to 7.03 g H_2O/100 g solid, and from 0.01 to 4.26 g H_2O/100 g solid for the UGP and PGP, respectively. On the other hand, for a small increase within the high water activity region ($0.704 \leq a_w \leq 0.939$) at 20 °C, the EMC increased significantly from 4.26 to 18.51 g H_2O/100 g solid for the UGP and from 7.03 to 12.12 g H_2O/100 g solid for the PGP. Within the range of temperatures studied, the critical a_w for UPG and PGP lies between 0.60 and 0.70. Above this range of a_w, the EMC increased significantly with a marginal increment in a_w. This shows that at $a_w > 0.70$, rapid spoilage of ginger powder may be expected.

The effect of temperature on EMC may also be seen in figures 1 and 2 for PGP and UPG, respectively. As the temperature increased at a constant a_w the EMC decreased. For example at $a_w = 0.805$, the EMC of PGP was 17.02 g H_2O/100 g solid at 20 °C and 12.77 g H_2O/100 g solid at 40 °C. Similarly, for the UGP the EMC was 14.89 g H_2O/100 g solid at 20 °C and 11.85 g H_2O/100 g solid at 40 °C. This implies that at any a_w, ginger powders become less hygroscopic with increase in temperature. Consequently, ginger powders may be expected to absorb more moisture at a lower temperature than at higher temperatures. Also at fixed moisture content, there was a consistent shift in a_w to higher values with an increase in temperature. An increase in temperature at constant moisture content causes a lowering of the isotherm curves. This phenomenon would lead to an increase in a_w, thereby making the product more susceptible to microbial spoilage (Labuza *et al.*, 1985; Bolin, 1980).

From the kinetic molecular theory, it could be argued that as the temperature increases, sorbed molecules gain kinetic energy and higher degree of freedom, thereby gaining an increased potential for escape of water from the sorbent surface. This causes the amount of sorbed water to decrease with an increase in temperature (Karel, 1975; Labuza *et al.*, 1985). Several researchers observed an increase in a_w with an increase in temperature. The researchers include Menkov and Durakova (2005) for defatted pumpkin seed powder, Menkov *et al.* (2005) for bean flour, Palou *et al.* (1997) for cookies and corn flaxes, Wang and Brennan (1991) for irish potatoes, Satimehin and Ezeike (2003) for gelatinized white yam, Alakali and Satimehin (2007) for bambara groundnut powders.. The authors postulated that as the temperature increased, the structure and constituents of the materials were affected resulting in surface plasticization, reduction in sorption sites and a decrease in the EMC. The implication is that at high storage temperatures, even though the EMC is constant, there would be a shift in water activity to values above the critical level for storage of the product. Hence the product will deteriorate at the higher temperatures than it would at the lower temperatures even when the EMC remains constant. From thermodynamic point of view, adsorption is an exothermic process: an increase in temperature would lead to a decrease in the amount of water adsorbed.

Typical effect of processing methods on moisture adsorption characteristics of ginger powder is shown in figure 3. The EMC values of PGP were lower than those of UGP samples at any

temperature and water activity studied. Powders of unpeeled ginger (UPG) were found to adsorb more moisture than PGP did. The high moisture content of UPG could be attributed to high porosity of the materials. The presence of peels in the powder may have created more air spaces and capillaries, which favors moisture adsorption. Another reason for the higher EMC of UGP could be the presence of pentosan in the peels, which is highly hydrophilic, favoring moisture retention. Nature provides peels to some products, amongst other things, to protect them from daily variations in relative humidity. That is why the peel always absorbs more water: it works like a "buffer" maintaining the inner parts of the product without suffering external relative humidity variations. Though peeling constitutes additional cost in ginger processing, the resulting powder is less hygroscopic and therefore more shelf-stable.
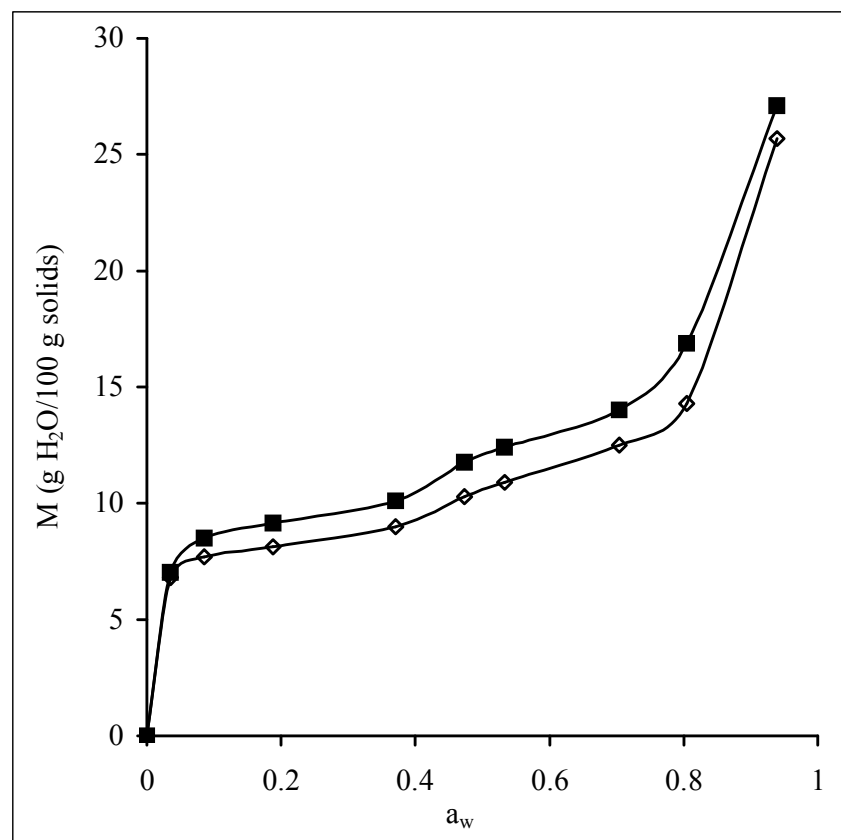

Figure 3. Typical comparison of moisture adsorption isotherms for
PGP (◊) and UPG (■) at 30 °C

4.2 Evaluation of Sorption Models

The parameters of the models tested are shown in table 1 and table 2 for peeled and unpeeled ginger powders, respectively. The percent root mean squares (%RMS) of error of the models are presented in table 3. From table 3, it can be seen that the %RMS for GAB and Oswin models were consistently less than 10 %, indicating their reliability in predicting moisture adsorption

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behavior of ginger powder. However the GAB model gave the lowest %RMS values and hence gave the best fit to experimental data. This agrees with Menkov and Durakova (2005) and Menkov *et al.* (2005) who fitted experimental moisture adsorption data for semi-defatted pumpkin seed flour and bean flour, respectively, using the models of Henderson, Oswin and GAB amongst others, and reported that GAB model gave very good fit. They also reported that Henderson model demonstrated the least accuracy to predict moisture adsorption behaviour of the two flours. In the present work, Henderson model similarly showed the least predictability of moisture adsorption in ginger powders.

Table 1. Parameter values for all models in adsorption of PGP

Models	Temperature (°C)			
	20	30	40	50
GAB				
G	128	265	4810	5210
K	0.368	0.864	0.844	0.829
M_o	0.058	0.052	0.046	0.043
S_o	203.778	182.700	161.617	151.077
Oswin				
A	8.270	8.769	7.764	6.650
B	0.084	0.087	0.075	0.088
Henderson				
A	-7.179	-6.642	-7.331	-6.310
B	2.689	2.444	2.899	2.579

Table 2. Model parameter for moisture adsorption of UGP

Models	Temperature (°C)			
	20	30	40	50
GAB				
G	243	264	5030	6020
K	0.377	0.879	0.923	0.943
M_o	0.063	0.062	0.053	0.052
S_o	221.345	217.832	186.211	182.700
Oswin				
A	8.671	11.336	7.668	7.579
B	0.092	0.055	0.085	0.083
Henderson				
A	-6.883	-8.379	-6.698	-6.901
B	2.533	2.930	2.998	2.711

Alakali J.S., Satimehin A.A. "Moisture Adsorption Characteristics of Ginger (*Zingiber officinale*) Powders". Agricultural Engineering International: the CIGR Ejournal. Manuscript 1286. Vol. XI. July, 2009.

Table 3. Percent root mean square (%RMS) of models

Sample	Temperature (°C)	%RMS GAB	Oswin	Henderson
PGP	20	5.6	3.9	11.0
	30	3.4	6.8	9.5
	40	4.6	6.1	11.4
	50	2.1	7.6	7.8
	Mean	3.9	6.1	9.9
UGP	20	2.7	5.1	12.2
	30	6.8	5.3	16.3
	40	4.9	7.9	9.3
	50	3.3	8.1	11.0
	Mean	4.4	6.6	11.3

4.3 Monolayer Moisture Content

The value of the monolayer moisture contents (M_o) indicates the amount of water that is strongly adsorbed to specified sites. It is considered the value at which a food is most stable. From table 1, the M_o for PGP decreased from 5.8 g H_2O/100 g solid at 20 °C to 4.3 g H_2O/100 g solid at 50 °C. Similarly, the M_o for UGP decreased from 6.0 g H_2O/100 g solid at 20 °C to 5.2 g H_2O/100 g solid at 50 °C (table 2). The values of M_o for both powders fell within the range of 4 to 11 g H_2O/100 g solid reported by Pérez-Alonso *et al.* (2006).

The decrease in monolayer moisture content with increase in temperature may be due to the reduction in the total number of sorption sites for water binding as a result of physical and or chemical changes in the product induced by temperature rise (Mazza, 1982). Also according to Palou *et al*. (1997), Palipane and Driscoll, (1992), Mok and Hittiarachchy (1990), an increase in temperature causes more activation of water molecules due to increase in energy level. This makes the water molecules less stable, thereby, favouring its break away from the binding sites of the food material. This in turn leads to a decrease in the monolayer moisture content.

Dried foods, in general, keep longer if they are held at low moisture contents. This can be attributed to their reduced oxidation and lowered chemical reaction (Bolin, 1980). However, even at low moisture storage, there exists optimum moisture content (monolayer), above which deterioration rate again accelerates (Labuza, 1968). For ginger powder, the monolayer moisture content can be used to estimate shelf stability and efficient use of energy in the drying process.

The monolayer moisture contents were used to determine the apparent area of sorption (S_o, m^2/g solid) using the following equation.

$$S_o = (1/M_s)N_oAM_o \qquad (22)$$

where M_s is the relative molecular mass of water, N_o is Avogadro's number (6.023×10^{23} molecules/mol), A is the surface area of one water-molecule (1.05×10^{-19} m^2). The S_o values are also shown in table 1 and table 2. The values were consistently higher for the UGP than the PGP.

As a direct linear function of M_o (equation 22), S_o naturally decreased with M_o but was found to have the following Arrhenius-type relationship with thermodynamic temperature.

$$S_o = S_o' \exp\left(\frac{-E_a}{RT}\right) \tag{23}$$

Equation (23) was linearized to give the following equation.

$$\ln(S_0) = \ln(S_0') - \left(\frac{E_a}{R}\right) \cdot \frac{1}{T} \tag{24}$$

Figure 4 is the graphical plot of equation (24), from which the intercept S'_0 and the slope E_a were obtained using direct linear regression. The regression analysis gave $S'_0 = 7.463$ m^2/g solid and $E_a = -805.211$ J/mol for the PGP; and for that of UGP, $S'_0 = 21.172$ m^2/g solid and $E_a = -576.160$ J/mol. In equation (24), S'_0 represents the apparent area of adsorption of water molecules at the triple point of water. At this temperature, the UGP presented nearly twice as large a surface area for moisture adsorption as did the PGP.
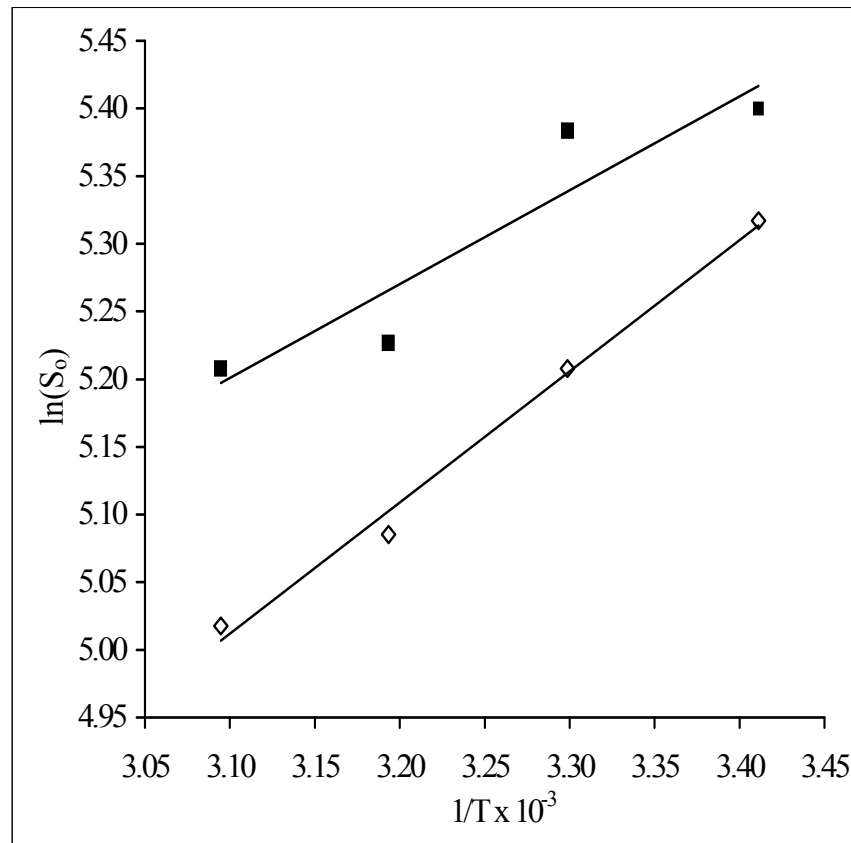

Figure 4. Arrhenius plot of S_0 versus 1/T for PGP (◊) and UGP (■)

The negative sign on the values of the activation energy of the first layer of water molecules indicated that the moisture adsorption process was exothermic. Monolayer moisture adsorption of PGP was more exothermic than the monolayer adsorption of those of UGP.

Alakali J.S., Satimehin A.A. "Moisture Adsorption Characteristics of Ginger (*Zingiber officinale*) Powders". Agricultural Engineering International: the CIGR Ejournal. Manuscript 1286. Vol. XI. July, 2009.

4.4 Isosteric Heat of Adsorption

The net isosteric heat of adsorption was obtained from the Clausius-Clapeyron equation (13) for PGP and UGP. The slopes of the plots of $\ln(a_w)$ versus $1/T$ gave the net isosteric heat for UGP (fig. 5) and PGP (fig. 6). The isosteric heat showed a marked decrease with increasing moisture content (fig. 7). Palou *et al.* (1997), Loong *et al.* (1995), Wang and Brennan, (1991), explained this decrease quantitatively. According to the authors, sorption initially occurs at the most active available sorption sites, giving rise to high interaction energy. As these sites become occupied, sorption occurs on the less active sites, giving rise to lower heat of sorption. In other words, as the moisture content increases, the available sites for moisture sorption reduce resulting in lower values of a_w and ΔH_{st}.
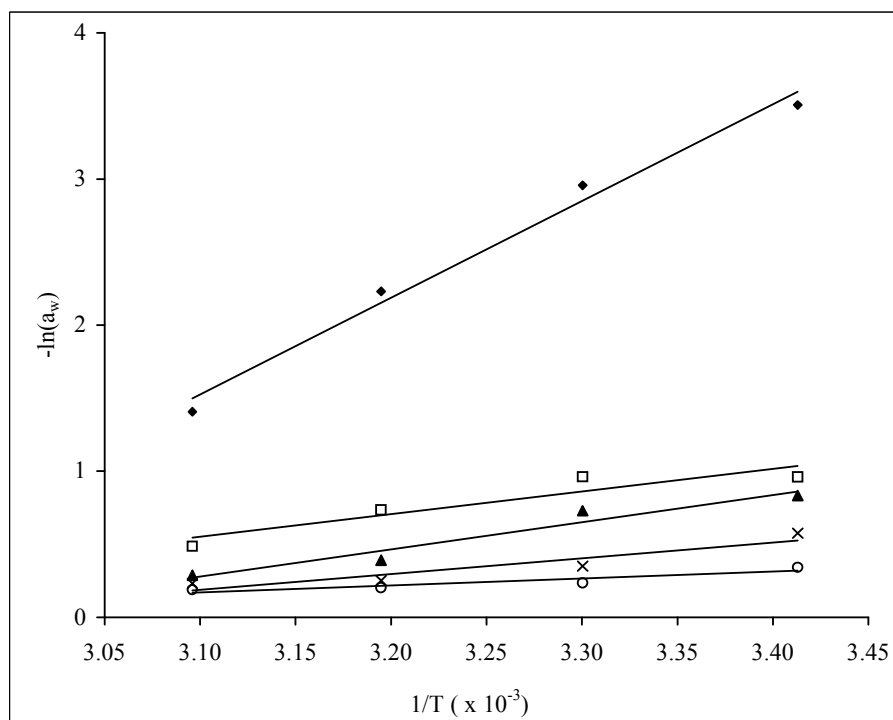

Figure 5. $Ln(a_w)$ vs $1/T$ for UGP at 8 (♦), 10 (□), 12 (▲), 14 (x) and 16 (o) g H_2O/100 g solid

Alakali J.S., Satimehin A.A. "Moisture Adsorption Characteristics of Ginger (*Zingiber officinale*) Powders". Agricultural Engineering International: the CIGR Ejournal. Manuscript 1286. Vol. XI. July, 2009.
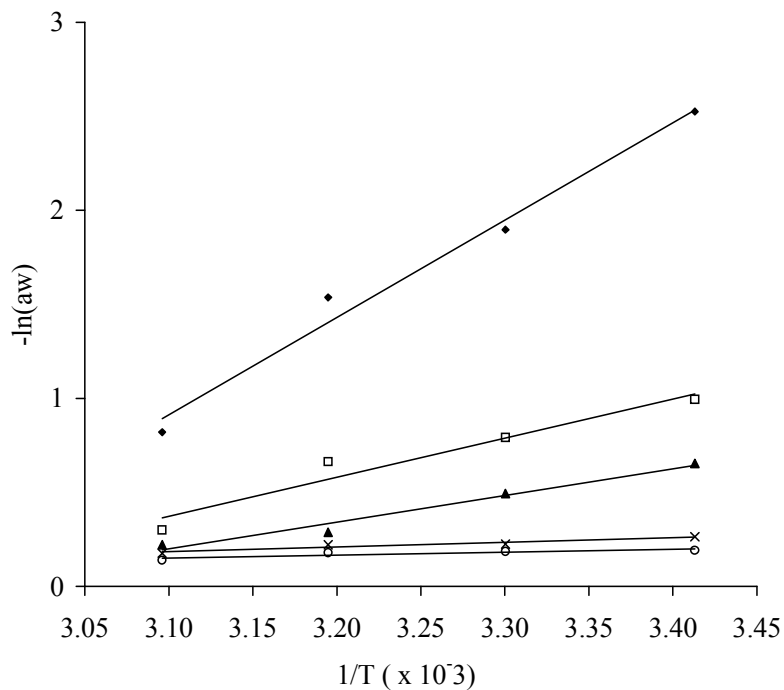
Figure 6. Ln(a_w) vs 1/T for PGP at 8 (◆), 10 (□), 12 (▲), 14 (x) and 16(o) g H_2O/100 g solid
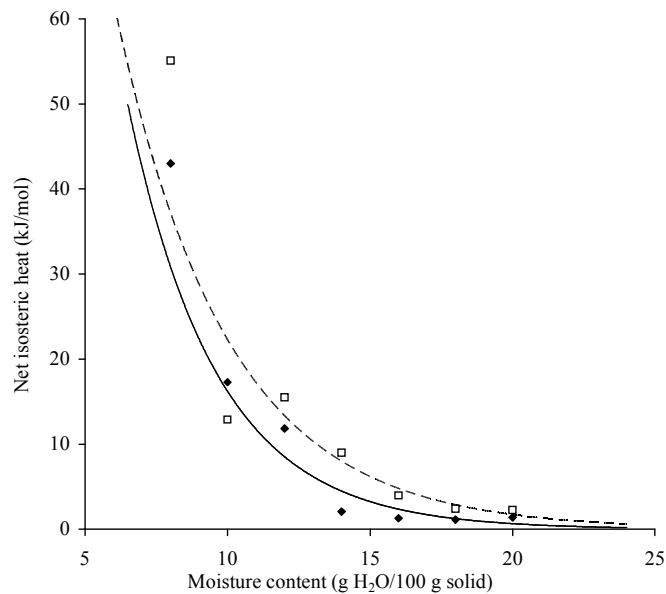
Figure 7. Net isosteric heat of adsorption against moisture content for UGP (□) and PGP (◆)

At low moisture, the high heat of adsorption is due in part to the greater resistant to moisture migration from the surface to the interior of a product (Cenkowski *et al*., 1992). It could happen also due to strong interaction between water molecules and the hydrophilic group of the food solid (Lim *et al*., 1995). According to Telis-Romero *et al.* (2005) elevated heats of sorption of

water at low moisture contents are an indication of strong water food-components interactions. Wang and Brennan (1991) also reported that the high heat of adsorption at lower moisture content could be attributed to the chemisorption on the polar sites and also to the strained hydrogen bonds in the food solid on dehydration.

Values of isosteric heat of adsorption of powders of ginger compare favorably with those of other foods substances. Satimehin and Ezeike (2003) reported, for gelatinised white yam, the value of 36.12 kJ/mol at moisture content of 6 g H_2O/100 g solid falling to 14.02 kJ/mol at moisture content of 12 g H_2O/100 g solid. Kiranoudis $et\ al$. (1992) reported for potatoes, the value of 34.80 kJ/mol at 6 g H_2O/100 g solid falling to 7.30 kJ/mol at 20 g H_2O/100 g solid.

The value of the isosteric heat of the first molecule (ΔH_o) and the characteristic moisture contents (M_{ch}) based on equation (15) are shown in table 4. The high ΔH_o and low M_{ch} for PGP gave an indication of loosed moisture bonds and the relative ease of moisture removal from peeled ginger compared to unpeeled ginger. Predictive models for the isosteric heat of adsorption of PGP and UGP, therefore, are as follows.

For PGP: $\Delta H_{st} = 403.830\exp(-0.322M)$ $(R^2 = 0.867)$ (25)

For UGP: $\Delta H_{st} = 288.310\exp(-0.256M)$ $(R^2 = 0.921)$ (26)

The above models can be used to estimate the energy requirement for peeled and unpeeled ginger drying. The models will also serve as valuable tool for optimum process and equipment design.

4.5 Guggenhiem Constant and Enthalpy of Sorption

The GAB thermodynamic derivatives based on equations (16) and (17) are summarized in table 5. The Guggenhiem constants (G and K) associated with monolayer and multilayer moistures, respectively, exhibited a defined trend showing an increase with temperature. G showed greater temperature dependence than K. This indicated that both monolayer and the multilayer moisture contents became more entropic with increase in temperature, thereby giving rise to increased values of G and K with increasing temperature. However, G was more entropic and K more enthalpic. The UGP exhibited higher G and K values than PGP. This could be due to the higher monolayer moisture (M_o) of the UGP.

The difference between the enthalpy of the monolayer and multiplayer (ΔH_G) were positive for both PGP and UGP (table 2). This suggested that less energy was needed to overcome sorption energy of the multilayer water in the materials than for pure water. The difference between the enthalpy of sorption of water and the multilayer (ΔH_K) were positive. Similarly, the enthalpy of sorption of the monolayer (H_m) was higher compared to that of the monolayer on top of the multilayer (H_n) for both samples. This suggested that stronger bonds existed between the solid and the monolayer water molecules than between monolayer and subsequent multilayer water molecules. This observation was also made in the report of Diosady $et\ al$. (1996) on canola oil.

Table 4. Regression parameters of the relationship between ΔH_{st} and moisture content of ginger powders.

Regression parameters	Peeled ginger powder	Unpeeled ginger powder
ΔH_o	59.695 kJ/mol	72.042 kJ/mol
M_{ch}	4.155 g H_2O/100 g solid	4.058 g H_2O/100 g solid
R^2	0.985	0.926

Table 5: GAB thermodynamic derivatives for PGP and UGP

| Sample	M_o (g H_2O/ g solid)	T (°C)	G (J/mol)	ΔH_G (J/mol)	K (J/mol)	ΔH_K (J/mol)	H_m (J/mol)	H_n (J/mol)	h_{fg} (J/mol)
PGP	0.058	20	6.67	6.53	2.04	1.30	147.82	141.29	139.99
	0.052	30	14.72	6.53	3.56	1.30	148.83	142.33	141.01
	0.047	40	267.22	6.53	4.61	1.30	149.84	143.31	142.02
	0.043	50	289.44	6.53	4.80	1.30	150.85	144.32	143.29
UGP	0.063	20	13.50	5.80	2.09	1.27	145.96	141.27	139.99
	0.061	30	14.89	5.80	4.88	1.28	146.81	142.32	141.01
	0.053	40	279.44	5.80	5.13	1.28	147.82	143.29	142.02
	0.052	50	334.44	5.80	5.24	1.28	148.83	144.29	143.29
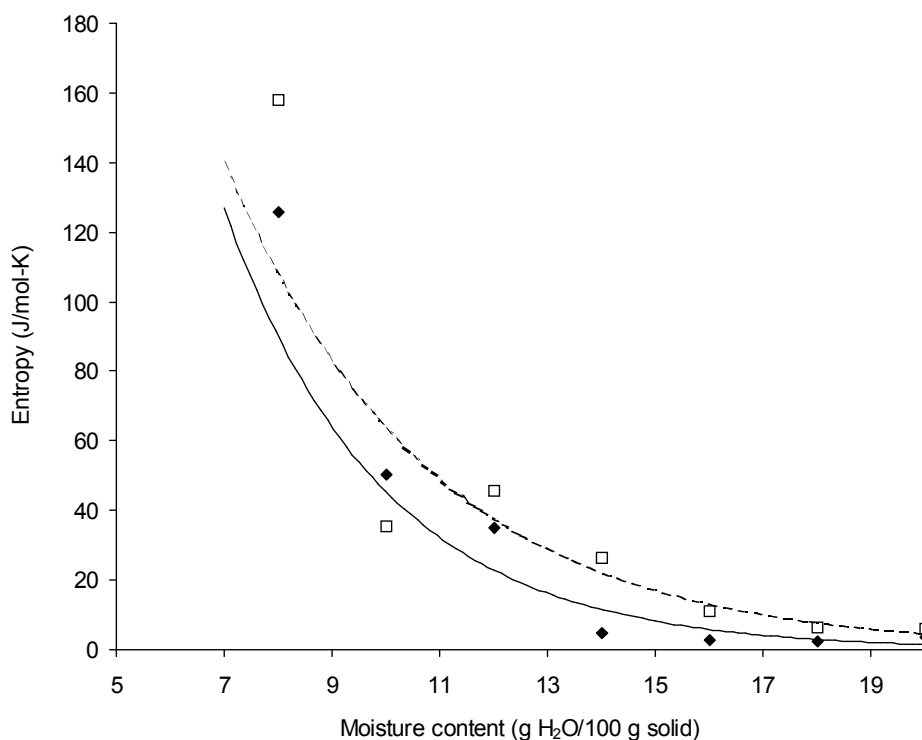
Figure 8. Entropy versus moisture content for UGP (□) and PGP (◆)

Alakali J.S., Satimehin A.A. "Moisture Adsorption Characteristics of Ginger (*Zingiber officinale*) Powders". Agricultural Engineering International: the CIGR Ejournal. Manuscript 1286. Vol. XI. July, 2009.

4.6 Entropy of Adsorption

The entropy of adsorption (ΔS^o) was determined based on equation (20), and found to decrease with moisture content (fig. 8). Entropy of adsorption was generally higher in the powders of unpeeled ginger (UGP) than in powders of peeled ginger (PGP). In the moisture content range of 8 to 20 g H_2O/100 g solid, the entropy of sorption of UPG decreased from 158.18 to 6.23 J/mol·K, and that of PGP decreased from 125.72 to 2.496 J/mol·K. Ariahu *et al.* (2006) explained that at low moisture content, water absorbs on the most accessible location on the external surface of the solid. As the moisture content increases the polymer swells, thereby opening up new higher energy sites for water binding. In addition, the water molecules become more mobile with higher degree of freedom resulting in higher entropy of sorption. At low moisture content however, the water molecules are tightly bound by physical and chemosorption forces leading to a loss of degree of freedom and low entropy of sorption.

5. CONCLUSIONS

Moisture sorption isotherms of ginger exhibited S shapes described as type II, typical of foodstuff. The EMC values of PGP and UGP increased with increasing water activity and decreased with increasing temperature. At any given temperature and water activity, UGP absorbed more moisture than PGP. The UGP showed higher monolayer moisture content than PGP and was found to be less shelf-stable. The isosteric heat of adsorption of powders of both peeled and unpeeled ginger decreased with increasing moisture content. This indicated that at low moisture contents, there were strong interactions between moisture and the solid matrix of the ginger powders. At constant moisture content, the net isosteric heat of sorption of the UGP was higher than that of PGP. On the other hand, the isosteric heat of sorption of the first molecule of water (ΔH_o) of PGP was higher than that of UGP. The characteristics moisture content (M_{ch}), was lower in powders of the peeled than unpeeled ginger. This gave an indication of relative ease of drying peeled ginger. The GAB monolayer constant (G) showed greater temperature dependence than the multilayer constant (K). Entropy decreased exponentially as the product adsorbed more moisture. However, entropy of the powders of UGP was generally higher than that of PGP at the same moisture content.

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