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Thermodynamic analysis of sorption isotherms of cassava (*Manihot esculenta*)

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Abstract Sorption isotherms of cassava were determined experimentally using a static gravimetric method at 30, 45 and 60 °C and within the range of 0.10–0.90 water activity. At a constant water activity, equilibrium moisture content *decreased* with increasing temperature. The equilibrium moisture content *increased* with increasing water activity at a given temperature. The experimental results were modelled using seven sorption models *using non-linear regression technique*. Results *demonstrated* that the GAB model *adequately predicted* equilibrium moisture content of cassava for the range of temperatures and water activities studied. The thermodynamic functions such as net isosteric heat of sorption, differential entropy of sorption, net integral enthalpy and entropy were evaluated to provide an understanding of the properties of water and energy requirements associated with the sorption behaviour. Net isosteric heat and differential entropy decreased with increasing equilibrium moisture content. The net integral enthalpy decreased while net integral entropy increased with increasing equilibrium moisture content. Net integral entropy was negative in value. All thermodynamic functions were adequately characterised by a power law model. The point of maximum stability was found between 0.053 and 0.154 kg water/kg db for cassava.

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Introduction

Cassava (*Manihot esculenta*) is a perennial shrub of the Euphorbiaceae family, native of Guyana. It is now widely cultivated and harvested as annual plant in the tropical and subtropical regions. Cassava is becoming an increasingly important *crop* in animal feed and human diet in West Africa (Olufayo and Ogunkunle 1996). Cassava tubers are processed in various ways for human consumption.

Cassava has a moisture content of 63 % wet basis at harvest. Therefore, they cannot be preserved for more than a few days under ambient conditions. Compared to fresh products which can only be kept for a few days under ambient conditions, dry products can be stored for months or even years without appreciable loss of nutrients (Shivhare et al. 2000; Mwithiga and Olwal 2005).

However, the knowledge of sorption isotherms is essential for various foodstuff processes such as drying, storage and packaging. Sorption isotherms describe the relationship between the equilibrium moisture content and the water activity at constant temperatures. They give information about the water sorption mechanism and interactions between food components and water. They are also extremely important in modelling of the drying process, in design and optimisation of drying equipment, in predicting shelf-life stability, in determining critical moisture, in selecting appropriate packaging material and water activity for acceptability of products that deteriorate mainly by moisture gain (Van den Berg and Bruin 1981; Gal 1987; Palou et al. 1997; Arora et al. 2003; Kaymak-Ertekin and Gedik 2004).

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Relevant work has been carried out on sorption isotherms characteristics of foodstuffs

(Mir and Nath 1995; Ayranci 1995; Myhara et al. 1998; Tsami et al. 1999; Ahouannou et al. 2000; Talla et al. 2001; Lahsani et al. 2003; Talla et al. 2005; Kaur et al. 2006; Yazdani et al. 2006; Vishwakarma et al. 2007; Jain et al. 2010; Jagadish et al. 2010; Chenlo et al. 2011).

Many empirical and semi-empirical mathematical models for description of the sorption behaviour of foodstuffs are available in literature. Criteria used for selecting the most appropriate sorption model are the degree of fit to the experimental data and the simplicity of the model (Kaymak-Ertekin and Gedik 2004; Basu et al. 2006; Chen and Weng 2010; Shafiq Alam and Singh 2011).

Knowing the sorption isotherms at different temperatures makes it possible to calculate the thermodynamic functions such as net isosteric heat, differential entropy, net integral enthalpy and entropy. The thermodynamic functions of water sorption in dried foodstuffs have drawn interest because it provides a more through interpretation of the sorption isotherm phenomenon and helps to understand better the sorption mechanism (Beristain et al. 2002; Pérez-Alonzo et al. 2006). The net isosteric heat of sorption can be used to estimate the energy requirements of drying and provides important information on the state of water in foodstuffs. The differential entropy of sorption is proportional to the number of available sorption sites at a specific energy level (Togrul and Arslan 2006; Rosa et al. 2010). Net integral enthalpy and entropy are used to explain the modes of moisture sorption by foodstuffs.

The objectives of this study are to determine the experimental sorption isotherms of cassava at 30, 45 and 60 °C, to evaluate the best sorption isotherm model to fit experimental data and to determine the thermodynamic functions such as net isosteric heat, differential entropy, spreading pressure, net integral enthalpy and entropy for the sorption isotherms of cassava.

Materials and methods

Experimental procedure

The static gravimetric method of the saturated salts solutions *was* used for adsorption and desorption isotherms determination. Ten saturated salt solutions selected to give different water activities in the range of 0.110–0.900 were used. These include: LiCl, KCH$_3$CO$_2$, MgCl$_2$, K$_2$CO$_3$, Mg(NO$_3$)$_2$, NaBr, SrCl$_2$, NaCl, KCl and BaCl$_2$. The water activity values of the saturated salt solutions at different experimental temperatures were taken from data reported by Kiranoudis et al. (1993) and given in Table 1.

The static gravimetric is a method where diffusion is the only way of mass transfer between the product and the surrounding air. The air relative humidity is fixed by contact with saturated salts solution whose water vapour pressure at a given temperature is perfectly known. This method is commonly used for product sorption isotherms determination (Kouhila et al. 2001; Lahsani et al. 2003; Talla et al. 2005; Yazdani et al. 2006; Brett et al. 2009; Singh et al. 2011) and is recommended by the COST 90 project (Wolf et al. 1985).

The samples were kept in triplicate in desiccators containing saturated salt solutions and placed in a temperature controlled cabinet, with an accuracy of ±1 °C at the selected temperatures 30 °C, 45 °C and 60 °C. For adsorption, the samples were pre-dried in a vacuum oven. The samples were weighed on an electronic balance with an accuracy of 0.01 g (Metter PL 1200 digital) at regular intervals until the equilibrium reached.

The cassava used in this study was purchased from the local retail market. The initial moisture content was determined by the oven-drying method for 24 h at 105 °C. Initial moisture content of cassava was 1.70 kg water/kg dry basis.

Data analysis and thermodynamic properties

Sorption isotherm

The relationship between the equilibrium moisture content and the water activity of the product *was* predicted by using the equations representing the models commonly used in foodstuff. These models which incorporate the temperature effect have been adopted as standard equations by the ASAE for the description of sorption isotherms (ASAE 1997). In this study, the eight isotherm models used to fit the experimental data are presented in Table 2.

Table 1 Water activity values of the saturated salt solutions at three temperatures

Saturated salt solutions	Temperatures (°C)		
	30	45	60
LiCl	0.113	0.112	0.110
KCH$_3$CO$_2$	0.216	0.195	0.160
MgCl$_2$	0.324	0.311	0.293
K$_2$CO$_3$	0.432	0.432	0.432
Mg(NO$_3$)$_2$	0.514	0.469	0.440
NaBr	0.560	0.520	0.497
SrCl$_2$	0.691	0.640	0.580
NaCl	0.751	0.745	0.745
KCl	0.836	0.817	0.803
BaCl$_2$	0.900	0.880	0.840

The constants were estimated by fitting the mathematical model to the experimental data, using a non-linear regression analysis with Microsoft Excel 2007 software. The quality of the fitting of different models was evaluated by calculating the correlation coefficient (r^2), the mean relative percentage deviation modulus E in % and the root mean square error (RMSE) between the experimental and predicted equilibrium moisture content (Boquet et al. 1978; Basu et al. 2006):

$$E = \frac{100}{N} \sum_{i=1}^{N} \frac{\left|X_{eq,exp} - X_{eq,pre}\right|}{X_{eq,exp}} \quad (1)$$

$$RMSE = \left[\frac{1}{N} \sum_{i=1}^{N} \left(X_{eq,exp} - X_{eq,pre}\right)^2\right]^{\frac{1}{2}} \quad (2)$$

where N is the number of observations; $X_{eq,exp}$ and $X_{eq,pre}$ are the experimental and predicted values of the equilibrium moisture content, respectively.

The mean relative percentage deviation modulus is widely adopted throughout the literature, with a modulus value below 10 % indicative of a good fit for practical purposes (Lomauro et al. 1985; Kaymak-Ertekin and Gedik 2004). In the same way, the smaller the RMSE value, the better the fit of the model.

According to Kaleemullah and Kallappan (2004), Aviara et al. (2004) and Basu et al. (2006), statistical parameters like r^2, E and RMSE may not be sufficient evidence for the goodness of fit of a moisture sorption model based on experimental data, but the nature of the residual plots should be considered in addition. A model was considered acceptable if the residuals ($X_{eq,exp} - X_{eq,pre}$) are uniformly scattered around the horizontal value of zero, showing no systematic tendency towards a clear pattern.

In the GAB model, X_m is the moisture content corresponding to the formation of a monomolecular layer on the internal surface; G is a constant related to the heat of sorption of the first layer on primary sites and K is a factor correcting properties of the multi-layer molecules with

respect to the bulk liquid. The influence of temperature on GAB constants G and K can be expressed with Arrhenius type equations (Bellagha et al. 2005):

$$G = G_0 \exp\left(\frac{\Delta H_G}{RT}\right) \text{ where } \Delta H_G = H_m - H_n \quad (3)$$

$$K = K_0 \exp\left(\frac{\Delta H_K}{RT}\right) \text{ where } \Delta H_K = H_L - H_n \quad (4)$$

where G_0 and K_0 are the pre-exponential factors, H_m is the sorption heat of the monolayer, H_n is the sorption heat of the multi-layer, H_L is the heat of condensation of water vapour (H_L=43.53 KJ.mol^{-1} at the average temperature 35 °C within the investigate range 25–45 °C), R is the universal gas constant (R=8.314 J.mol^{-1} K^{-1}) and T is the absolute temperature.

Bizot (1983) transformed the GAB equation into a quadratic equation:

$$\frac{a_w}{X_{eq}} = Aa_w^2 + Ba_w + C \quad (5)$$

Where A, B and C are the coefficients dependent of temperature.

By combining Eq. (5) and GAB equation, other expressions to estimate X_m, G and K may be considered:

$$X_m = \frac{1}{\left(B^2 - 4AC\right)^{\frac{1}{2}}} \quad (6)$$

$$G = \frac{2}{1 - \left(\frac{B^2}{B^2 - 4AC}\right)^{\frac{1}{2}}} \quad (7)$$

$$K = \frac{\left(B^2 - 4AC\right)^{\frac{1}{2}} - B}{2C} \quad (8)$$

Table 2 Sorption models used for fitting experimental data

Name of the model	Range of a_w	Mathematical expression
GAB (Guggenheim-Anderson-de Boer) (Van den Berg and Bruin 1981)	$a_w < 0.95$	$X_{eq} = \frac{X_m G K a_w}{(1 - K a_w)[1 + (G-1) K a_w]}$
BET (Brunauer et al. 1938)	$a_w < 0.50$	$X_{eq} = \frac{X_m C a_w}{(1 - a_w)[1 + (C-1) a_w]}$
Halsey (Hasley 1948)	$0.10 < a_w < 0.80$	$X_{eq} = \left[\frac{A}{\ln(1/a_w)}\right]^{\frac{1}{B}}$
Oswin (Oswin 1946)	$0.10 < a_w < 0.80$	$X_{eq} = A\left[\frac{a_w}{1 - a_w}\right]^{B}$
Smith (Smith 1947)	$0.50 < a_w < 0.95$	$X_{eq} = B + A \ln(1 - a_w)$
Iglesias-Chirife (Iglesias and Chirife 1981)	$0.10 < a_w < 0.80$	$X_{eq} = A + B\left[\frac{a_w}{1 - a_w}\right]$
Kuhn (Kuhn 1967)	$a_w < 0.50$	$X_{eq} = B + \frac{A}{\ln(a_w)}$

The BET model can be rearranged as:

$$\frac{a_w}{(1 - a_w)X_{eq}} = \alpha + \beta a_w \tag{9}$$

with

$$X_m = \frac{1}{\alpha + \beta} \tag{10}$$

$$C = \frac{\alpha + \beta}{\alpha} \tag{11}$$

Treatments of sorption data according to the BET (values for a_w up to 0.5) and GAB (values for a_w up to 0.95) models allow the evaluation of monolayer moisture content values, X_m, of foodstuffs. The prediction of X_m values is important since deterioration of foodstuffs is very small below X_m. This is because water is strongly bound to the foodstuff below X_m and is not involved in any deteriorative reaction either as solvent or as one of the substrates (Ayranci and Duman 2005). Once the monolayer moisture content was known, the water surface area of product can be determined by the following Eq. (11) (Rosa et al. 2010). The specific surface area plays an important role in determining the water binding properties of particulate products.

$$S_a = X_m \frac{1}{M_{H_2O}} A_{H_2O} N_A = 3.53 \times 10^3 X_m \tag{12}$$

where S_a is the product surface area ($m^2.g^{-1}$), X_m is the monolayer moisture content ($kg.kg^{-1}$ dry basis), M_{H_2O} is the molecular weight of water (18 $g.mol^{-1}$), N_A is Avogadro's number (6×10^{23} molecules.mol^{-1}) and A_{H_2O} is the area of one water molecule (1.06×10^{-19} m^2).

Isosteric heat of sorption

Isosteric heat of sorption or differential enthalpy is the amount of energy required to change unit mass of a product from liquid to vapour at a particular temperature and water activity (Aviara et al. 2002). The net Isosteric heat of sorption is defined as the isosteric heat of sorption minus the latent heat of the pure water vaporisation. It can be computed from experimental sorption isotherm data using the Clausius-Clapeyron equation in the form (Kaya and Kahyaoglu 2007; Singh et al. 2011; Chenlo et al. 2011):

$$\left[\frac{d \ln(a_w)}{d\left(\frac{1}{T}\right)}\right]_{X_{eq}} = -\frac{Q_{st} - L_v}{R} = -\frac{q_{st}}{R} \tag{13}$$

where q_{st} is the net isosteric heat of sorption ($kJ.mol^{-1}$); Q_{st} is the isosteric heat of sorption ($kJ.mol^{-1}$); L_v is the latent heat of the pure water vaporisation ($kJ.mol^{-1}$).

The aforementioned procedure assumes that q_{st} is independent of temperature; although this is not always true, it has often been accepted (Iglesias et al. 1989). The application of this method requires data at least at two or more experimental temperatures. On the other hand the integrating of Eq. (13) between the two equilibrium states (T_1, a_{w1}) and (T_2, a_{w2}) for any arbitrary constant moisture content, X, leads to Eq. (14):

$$q_{st} = R \frac{T_1 T_2}{T_2 - T_1} \ln\left(\frac{a_{w2}}{a_{w1}}\right) \tag{14}$$

Where a_{wi} is the measurement of water activity at the absolute temperature T_i for constant moisture content.

Differential entropy

Entropy change plays an important role in the energy analysis of food processing systems. The differential entropy or sorption entropy is proportional to the number of available sorption sites at a specific energy level (Togrul and Arslan 2006). The differential entropy (ΔS) was obtained by fitting Eq. (15) to equilibrium moisture content data from the best-fitting equation (Madamba et al. 1996).

$$\ln(a_w) = -\frac{q_{st}}{RT} + \frac{\Delta S}{R} \tag{15}$$

The net isosteric heat of sorption and differential entropy can be calculated from Eq. (15) by plotting $\ln(a_w)$ versus $1/T$, for given a moisture content and then determining the slope ($-q_{st}/R$) and the linear coefficient ($\Delta S/R$).

Enthalpy-entropy compensation theory

The compensation theory was further used to evaluate the effect of temperature on the sorption behaviour. It proposes a linear relationship between q_{st} and ΔS (McMinn and Magee 2003):

$$q_{st} = T_\beta \Delta S + \Delta G_\beta \tag{16}$$

The isokinetic temperature, T_β, has an important physical meaning as it represents the temperature at which all reactions in the series proceed at the same rate. The free energy, ΔG_β, at temperature T_β provides a criterion to estimate if the water sorption process is spontaneous ($-\Delta G_\beta$) or no ($+\Delta G_\beta$).

Since there is a high degree of linear correlation between enthalpy and entropy, the compensation theory was assumed to be valid for sorption (Madamba et al. 1996; Vishwakarma et al. 2011). To corroborate the compensation theory, a statistical analysis test (Eq. (17)) was proposed by Krug et al. (1976a, b). This involves a comparison of the isokinetic temperature (T_β) with the harmonic mean temperature

(T_{hm}). The compensation theory only applies if $T_\beta \neq T_{hm}$.

$$T_{hm} = \frac{n}{\sum_{i=1}^{n} \left(\frac{1}{T_i}\right)} \quad (17)$$

Spreading pressure

The spreading pressure is the two-dimensional analogue of pressure, having units of force per unit length, akin to surface tension. It can be viewed as the force in the plane of the surface that must be exerted perpendicular to each unit length of edge to keep the surface from spreading (Smith et al. 2001). Skaar and Babiak (1982) used the spreading pressure concept as the driving force in developing transport models during diffusion in porous solid. The spreading pressure (surface potential) which is the surface excess free energy is calculated using an analytical procedure described by Iglesias et al. (1976):

$$\pi = \frac{K_B T}{A_{H_2O}} \int_0^{a_w} \frac{\theta}{a_w} da_w \quad (18)$$

with the moisture ratio θ is:

$$\theta = \frac{X_{eq}}{X_m} \quad (19)$$

where K_B is the Boltzmann's constant ($K_B = 1.38 \times 10^{-23}$ JK^{-1}) and π is the spreading pressure (J.m^{-2}).

The value of $a_w = 0$ will make the integral of Eq. (18) to be indeterminate. Therefore, the GAB model (Eq. (20)) was used since the calculation of the integral in Eq. (18) changes from a numerical procedure to assume an empirical relationship between water activity and equilibrium moisture content.

$$\frac{a_w}{X_{eq}} = \frac{K}{X_m}\left(\frac{1-G}{G}\right)a_w^2 + \frac{1}{X_m}\left(\frac{G-2}{G}\right)a_w$$
$$+ \frac{1}{X_m G K} \quad (20)$$

Substituting Eq. (20) into Eq. (18), rearranging and then integrating gives the spreading pressure at different temperatures on the basis of surface area per sorption site or area per one molecule of water on each sorption site as:

$$\pi = \frac{K_B T}{A_{H_2O}} \ln\left[\frac{1 + Ka_w(G-1)}{1 - Ka_w}\right] \quad (21)$$

Net integral enthalpy and entropy

The net integral enthalpy represents the total energy available to do work. It provides an indication of the binding strength of water molecules to the solid, and has some

bearings on the energy balance of drying and freezing operations (Gal 1975). The net integral enthalpy (q_{in}), a measure of the food-water affinity, was determined in a similar manner as the isosteric heat but at a constant spreading pressure (Togrul and Arslan 2007).

$$\left[\frac{d\ln(a_w)}{d\left(\frac{1}{T}\right)}\right]_\pi = -\frac{q_{in}}{R} \quad (22)$$

A plot of $\ln(a_w)$ versus 1/T at constant spreading pressure gives the net integral enthalpy from the slope.

The net integral entropy describes the degree of disorder and randomness of motion of water molecules. It quantifies the mobility of the adsorbed water molecules, and indicates the degree to which the water-substrate interaction exceeds that of the water molecules (Togrul and Arslan 2006). The net integral entropy (ΔS_{in}) is given by (Togrul and Arslan 2006):

$$\Delta S_{in} = -\frac{q_{in}}{T} - R\ln\left(a_w^*\right) \quad (23)$$

where a_w^* is the geometric mean water activity obtained at constant spreading pressure at different temperatures.

Results and discussions

Sorption isotherm

The sorption isotherm representing the variation of the equilibrium moisture content with the water activity is plotted in Fig. 1 for cassava at various temperatures. The isotherm is *sigmoidal* as usually presented for foodstuff by Iglesias and Chirife (1982). This is typical of type II isotherms and has been reported for starchy products as potato (McMinn and Magee 2003), yellow dent corn (Samapundo et al. 2007), oat flour and rice flour (Brett et al. 2009), tea (Chen and Weng 2010), chestnut flour and starch (Chenlo et al. 2011), guar grains and splits (Vishwakarma et al. 2011). The equilibrium moisture content decreases with the temperature at constant water activity. Equilibrium moisture content increases also with increase in water activity for all temperatures. This behaviour may be attributed to the excitation states of molecules. At increased temperatures, molecules are in an increased state of excitation, thus increasing their distance decreases the attractive forces between them (Kaya and Aydin 2009). This leads to a decrease in the degree of water sorption at a given water activity with increasing temperature (Jamali et al. 2006). Whereas Mazza and Lemaguer (1980) suggested that increase in temperature induces physical and chemical changes in the product that can reduce the number of active sites for water binding. The temperature dependence of the equilibrium moisture content has an important practical bearing on chemical and microbiological
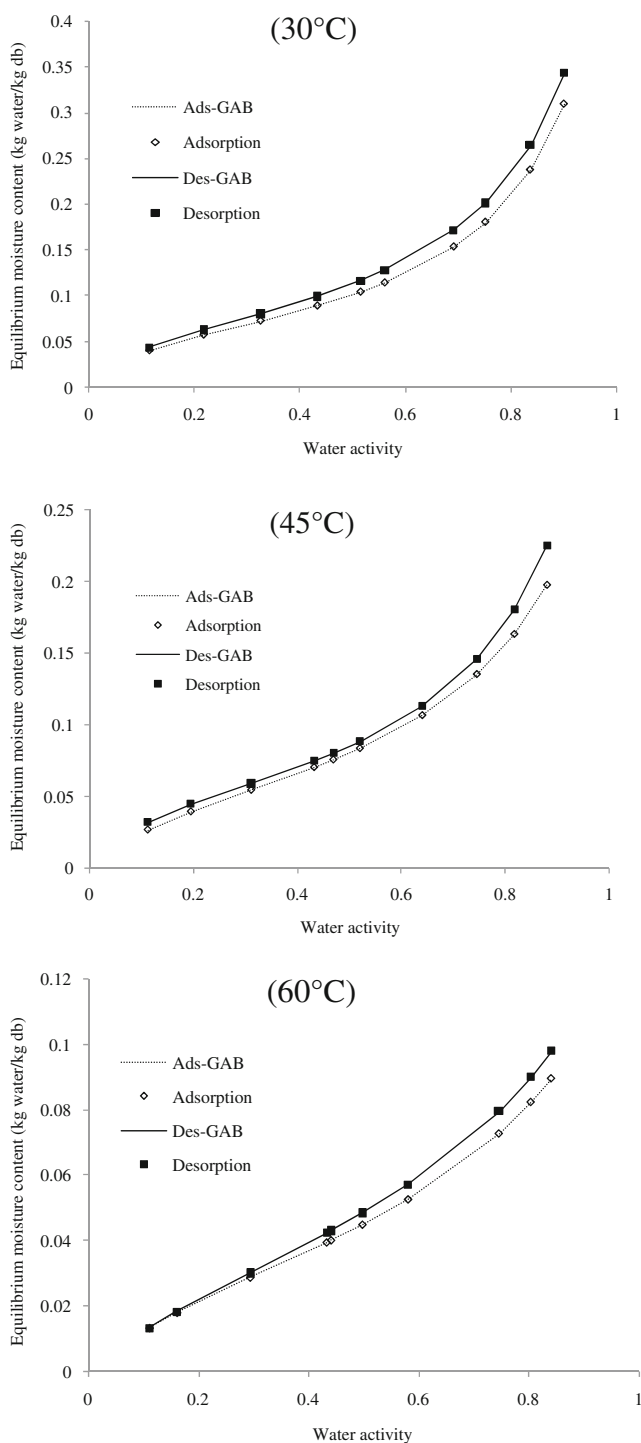
Fig. 1 Experimental adsorption and desorption isotherms of cassava at 30, 45 and 60 °C and estimated curves with GAB model

reactions associated with spoilage (Al-Muhtaseb et al. 2004). At the same moisture content, higher temperatures entail a higher water activity and consequently faster rates of deterioration (Van den Berg and Bruin 1981).

The comparison of the adsorption and desorption data are illustrated in Fig. 1. The desorption curves clearly lie above

the adsorption curves, forming the hysteresis loop. The hysteresis effect extends over the entire water activity range. Hysteresis is not fully understood (Al-Muhtaseb et al. 2004), although there is general agreement that some thermodynamically irreversible processes must occur during desorption or adsorption, or both. One theory used to explain hysteresis suggests that in the wet condition the polar sites in the molecular structure of the material are almost entirely satisfied by adsorbed water. The shrinkage that occurs upon drying draws them closer enabling them to satisfy each other. This reduces the water binding capacity during adsorption (Mohsenin 1986). Similar hysteresis phenomena have been reported for some foods (Johnson and Brennan 2000; Al-Muhtaseb et al. 2004; Togrul and Arslan 2007; Samapundo et al. 2007; Shafiq Alam and Singh 2011).

Table 3 shows the coefficients of the models fitted to the experimental adsorption and desorption data by non-linear regression, the mean relative percentage deviation modulus (E), the root mean square error (RMSE) and the correlation coefficient (r^2). All models presented correlation coefficients very close to unity indicating good fit to experimental data. The high value of r^2 at different temperatures showed that the good fit of the models is independent of temperature.

According to the results shown in Table 3, for temperatures from 30 to 60 °C and water activities from 0.10 to 0.90, it can be seen that the GAB model obtained the least mean relative percentage deviation modulus (E), least root mean square error (RMSE) and highest correlation coefficient (r^2) followed by BET and Smith model that showed very similar fitting parameters.

Plotting residuals of the models against water activity revealed that GAB model, BET model, Smith model, Kuhn model and Oswin model presented a random residual distribution and the other models, Halsey and Iglesias-Chirife model, a patterned residual distribution. According to these results, GAB model was considered the best model for predicting the equilibrium moisture content of cassava. The GAB model has a theoretical basis, while the other models are empirical or semi-empirical (Adebowale et al. 2007). According to Lomauro et al. (1985), the GAB model provides the best fit for more than 50 % of the fruits, meats and vegetables analysed. This model has been widely applied to describe equilibrium moisture content in foodstuffs, and was recommended by the European Project COST90 (Garcia-Pérez et al. 2008).

Monolayer moisture content (X_m) of cassava obtained using GAB and BET models are also given in Table 3. In the adsorption mode, X_m ranged from 6.16 to 3.66 g water/100 g dry basis and 5.55 to 2.64 g water/100 g dry basis for the GAB and BET models, respectively. In the desorption mode, X_m ranged from 6.96 to 4.21 g water/100 g dry basis and 6.24 to 2.93 g water/100 g dry basis for the GAB and

Table 3 Estimated values of constants for the different isotherm models

Models	Constants	Adsorption			Desorption		
		30 °C	45 °C	60 °C	30 °C	45 °C	60 °C
GAB	X_m	0.0616	0.0559	0.0366	0.0696	0.0536	0.0421
	G	12.9004	7.5707	5.6697	11.9016	10.9047	4.6800
	K	0.8939	0.8298	0.7498	0.8900	0.8731	0.7379
	r^2	0.999	0.999	1	0.999	0.999	1
	E (%)	0.035	0.018	0.008	0.034	0.028	0.009
	RMSE	0.00004	0.00005	0.000005	0.00007	0.00006	0.000004
BET	X_m	0.0555	0.0457	0.0264	0.0624	0.0454	0.0293
	C	15.1463	9.2251	7.1710	13.8745	13.0414	5.8703
	r^2	0.998	0.999	0.997	0.998	0.998	0.999
	E (%)	0.42	0.71	1.01	0.43	0.73	0.98
	RMSE	0.00039	0.00052	0.00046	0.00044	0.00063	0.00048
Halsey	A	0.0278	0.0264	0.0157	0.0337	0.0207	0.0209
	B	1.3927	1.2723	1.1962	1.3736	1.3831	1.1299
	r^2	0.995	0.973	0.937	0.994	0.986	0.929
	E (%)	2.58	5.23	7.72	2.91	3.64	8.62
	RMSE	0.0029	0.0055	0.0048	0.0038	0.0037	0.0059
Oswin	A	0.1042	0.0801	0.0442	0.1160	0.0824	0.0475
	B	0.468	0.509	0.536	0.475	0.466	0.568
	r^2	0.996	0.998	0.987	0.997	0.999	0.983
	E (%)	1.59	1.26	2.92	1.33	0.94	3.50
	RMSE	0.0024	0.0011	0.0020	0.0022	0.0006	0.0026
Smith	A	−0.129	−0.082	−0.038	−0.142	−0.085	−0.042
	B	0.006	0.022	0.019	0.008	0.021	0.020
	r^2	0.996	0.999	0.999	0.996	0.999	0.998
	E (%)	1.52	0.61	0.71	1.41	0.45	0.73
	RMSE	0.0034	0.0012	0.00089	0.0036	0.0013	0.0010
Iglesias-Chirife	A	0.048	0.035	0.019	0.053	0.038	0.015
	B	0.046	0.037	0.020	0.052	0.036	0.022
	r^2	0.973	0.944	0.929	0.972	0.954	0.906
	E (%)	6.87	10.65	11.98	7.15	8.72	15.28
	RMSE	0.0064	0.0069	0.0044	0.0073	0.0061	0.0076
Kuhn	A	−0.065	−0.055	−0.0323	−0.074	−0.052	−0.036
	B	0.012	0.004	0.0005	0.012	0.01	0.001
	r^2	0.988	0.988	0.987	0.987	0.987	0.983
	E (%)	1.32	2.20	2.57	1.39	1.83	5.70
	RMSE	0.0015	0.0015	0.0010	0.0016	0.0013	0.0020

BET models, respectively. The decrease in monolayer moisture contents with increase in temperature, as observed in this study, 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 (Iglesias and Chirife 1976). Also, according to Palipane and Driscoll (1992), it could be that with increase in temperature, the water molecules got activated due to an increase in their energy level, causing them to become less stable and to break away from the water binding sites of the food, thus decreasing the monolayer moisture content. These observations imply that the anticipated temperature

Table 4 Characteristic parameters of the GAB model

	G_0	K_0	ΔH_G (kJ.mol^{-1})	ΔH_K (kJ.mol^{-1})
Adsorption	0.0017	0.0377	22.77	10.73
Desorption	0.00038	0.0134	26.09	13.19

Table 5 Water surface area of cassava

Temperature (°C)	Adsorption S_a (m^2.g^{-1})	Desorption S_a (m^2.g^{-1})
30	217.55	245.76
45	185.75	197.36
60	129.23	148.65

of storage of the cassava would determine the optimum moisture content for maximum self stability.

Table 4 gives the results of the regression analysis of GAB model parameters. The positive value for ΔH_G in adsorption and desorption mode indicates that the sorption heat of water monolayer molecules (H_m) is higher than the sorption heat of water multilayer molecules (H_n). The positive value for ΔH_k in adsorption and desorption mode indicates that the condensation heat of water vapour (H_L is higher than the sorption heat of water multilayer molecules (H_n). The ΔH_G and ΔH_K values for desorption are higher than the values for adsorption in the case of cassava. The variation in enthalpy values between adsorption and desorption suggests a degree of irreversibility with respect to the water binding properties of the foodstuffs (McMinn and Magee 1999).

Table 5 presents the water surface area of cassava between 30 and 60 °C. It was estimated using Eq. (12) and the monolayer moisture contents of cassava obtained by GAB model. These results (Table 5) indicate that the availability of surface areas for hydrophilic binding decrease with increasing temperature. The calculated surface area values of cassava were within the range commonly obtained for foodstuffs (100–250 m^2.g^{-1}) (Cassini et al. 2006). Aguerre et al. (1989) and Calzetta et al. (2000) indicated that the large

surface area of many biopolymers is due to the existence of an intrinsic microporous structure in the foodstuffs.

Thermodynamic properties

Net isoteric heat of sorption

The net isoteric heats of adsorption and desorption of water at constant equilibrium moisture content were determined by applying Eqs. (13) and (14) to data calculated by using the GAB model that gave the best fitting of equilibrium moisture content data in the range of temperature from 30 to 60 °C. As can be observed in Table 6, the net isoteric heats for cassava at different equilibrium moisture contents from isotherms through the differential method (Eq. (13)) and by the integral method (Eq. (14)) are very close.

Figure 2 shows the net isoteric heat of adsorption and desorption of cassava as a function of equilibrium moisture content. It can be clearly seen that the net isoteric heat of adsorption and desorption decreased with increasing equilibrium moisture content. This decrease can be qualitatively explained by considering that sorption initially occurs at the most active sites, giving rise to the greatest interaction energy. As the equilibrium moisture content increases, the sites available for water sorption decrease, resulting in lower values of net isoteric heat (Tsami et al. 1990). Similar results have been reported for the foodstuffs in literature (Delgado and Sun 2002; Kaymak-Ertekin and Gedik 2004; Kaya and Kahyaoglu 2007; Rosa et al. 2010).

Comparison of the adsorption and desorption data shows that, at constant equilibrium moisture content, the net isoteric heat of desorption is higher than the corresponding adsorption value. This indicates that the desorption process

Table 6 Net isoteric heats of sorption and sorption entropy

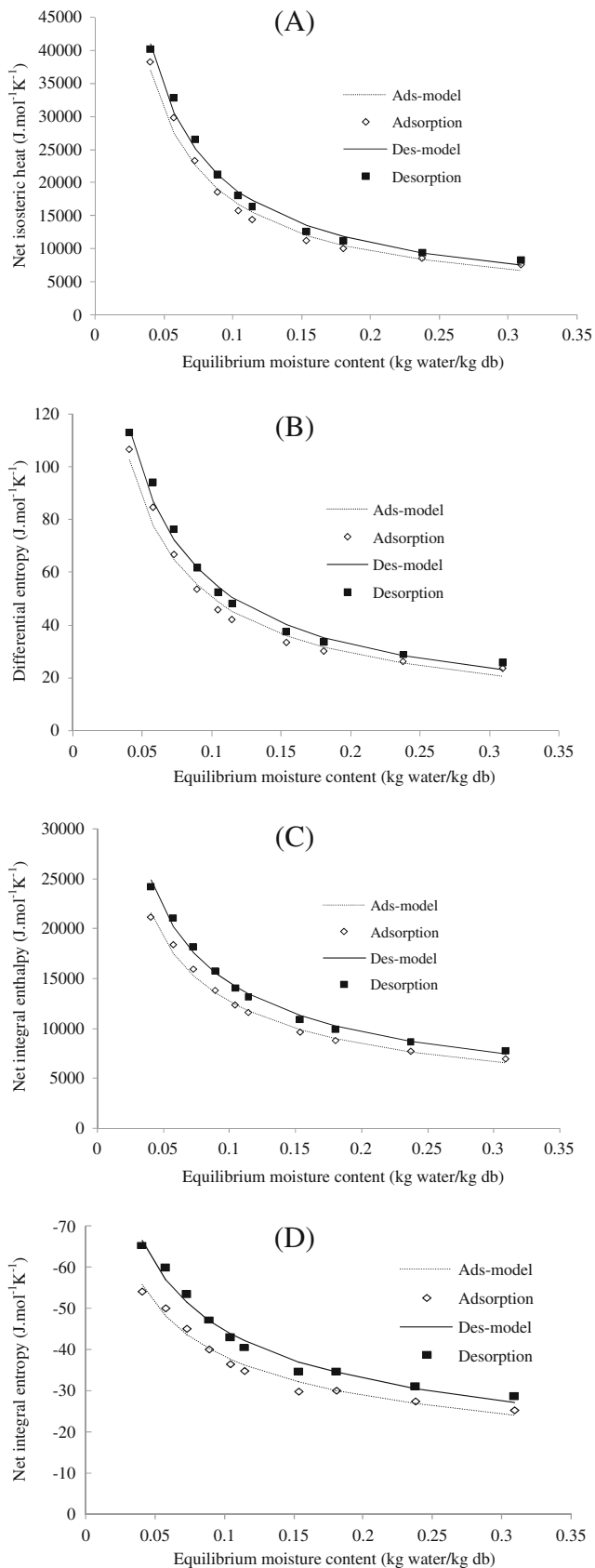| Equilibrium moisture content (kg water/kg db)	Adsorption			Desorption		
	Differential entropy (J.mol^{-1} K^{-1})	Net isoteric heat (kJ.mol^{-1} K^{-1})		Differential entropy (J.mol^{-1} K^{-1})	Net isoteric heat (kJ.mol^{-1} K^{-1})	
		Eq. (16)	Eq. (15)		Eq. (16)	Eq. (15)
0.0406	106.67	38.32	38.07	112.99	40.18	40.15
0.0577	84.72	29.86	29.70	94.03	32.82	32.82
0.0729	66.88	23.34	23.22	76.45	26.45	26.45
0.0894	53.71	18.58	18.48	61.84	21.24	21.23
0.1045	45.93	15.77	15.68	52.66	17.97	17.95
0.1145	42.21	14.41	14.33	48.16	16.36	16.34
0.1538	33.51	11.22	11.15	37.60	12.55	12.52
0.1806	30.29	10.03	9.96	33.68	11.12	11.09
0.2376	26.33	8.54	8.48	28.95	9.37	9.34
0.3094	23.75	7.57	7.52	25.91	8.24	8.21

Fig. 2 Net isosteric heat (a), differential entropy (b), net integral enthalpy (c) and net integral entropy (d) of adsorption and desorption of cassava with equilibrium moistent content

requires a greater amount of energy than adsorption as stated by Rizvi (1986) for rice, Wang and Brennan (1991) for potatoes, McMinn and Magee (2003) for potato, Kaymak-Ertekin and Gedik (2004) for grapes, apricots, apples and potatoes, Samapundo et al. (2007) for yellow dent corn. The net isosteric heat versus equilibrium moisture content results are adequately represented by a power law relation of the form:

Adsorption: $q_{st} = 2497.38\, X_{eq}^{-0.841}$ with $r^2 = 0.984$
Desorption: $q_{st} = 2807.36\, X_{eq}^{-0.836}$ with $r^2 = 0.988$

Differential entropy

The differential entropy of cassava versus equilibrium moisture content is shows in Fig. 2. The differential entropy decreases with increasing equilibrium moisture content. At low water activity range, a decrease in differential entropy values is possibly caused by the strongest binding sites with water molecules and the solid as suggested by McMinn and Magee (2003). Once again, the differential entropy of desorption is higher than the corresponding adsorption value, at constant equilibrium moisture content. The differential entropy data displays a strong dependence on equilibrium moisture content as stated by Kaya and Kahyaoglu (2007). The differential entropy versus equilibrium moisture content results are adequately represented by a power law relation of the form:

Adsorption: $\Delta S = 8.35\, X_{eq}^{-0.782}$ with $r^2 = 0.980$
Desorption: $\Delta S = 9.35\, X_{eq}^{-0.781}$ with $r^2 = 0.985$

Enthalpy-entropy compensation theory

Figure 3, representing q_{st} as a function of ΔS, shows a linear relation with a correlation coefficient $r^2 = 0.999$. Table 7
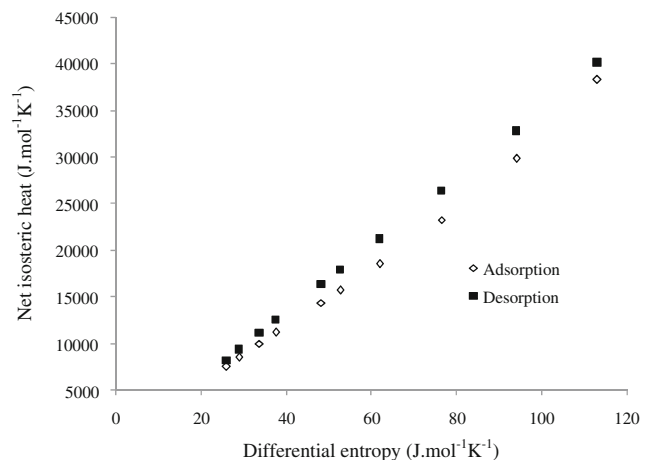

Fig. 3 q_{st} versus ΔS relationship for adsorption and desorption in cassava

gives the parameters T_β and ΔG_β (Eq. (16)) calculated from the data by linear regression. The adsorption data gives higher values than those for desorption.

Confirmation of the application of the compensation theory is provided by calculation of an harmonic mean temperature (T_{hm}) value of 317.66 K. For both adsorption and desorption $T_\beta \neq T_{hm}$. The compensation theory can also be applied and the water sorption in cassava is spontaneous ($\Delta G_\beta < 0$). Similar results for guar have been obtained by Vishwakarma et al. (2011).

Spreading pressure

The spreading pressure values (π) were evaluated using the analytical expression (Eq. (21)). The constants (G, K) in Eq. (21) were determined from the GAB model. The spreading pressure in adsorption and desorption process of cassava are represented in Fig. 4. The results shown that the spreading pressure increased with increasing water activity and, at a given water activity, decreased with increasing temperature. The trends of spreading pressures with respect to temperature and water activity for adsorption and desorption were similar to those determined by Fasina et al. (1999) for winged bean and gari, Aviara and Ajibola (2002) for melon seed and cassava, McMinn and Magee (2003) for potato.

Net integral enthalpy and entropy

The net integral enthalpy variations with respect to equilibrium moisture content are represented in Fig. 2. The net integral enthalpy of adsorption and desorption decreased with increasing equilibrium moisture content. The net integral enthalpy values for desorption were greater than those for adsorption at any equilibrium moisture content. The reason for such behaviour may be chain rupture or irreversible swelling (Togrul and Arslan 2006). The results are similar to those reported by Aviara and Ajibola (2002) for cassava, Togrul and Arslan (2006) for rice. While the net integral enthalpy of adsorption differed from the net enthalpy of desorption in magnitude, the net enthalpies of adsorption and desorption were qualitatively similar with regard to their functionality with equilibrium moisture content. The experimental net enthalpy data conform to a power law relation as represented by the equation:

Adsorption: $q_{in} = 3320.93\, X_{eq}^{-0.584}$ with $r^2 = 0.993$
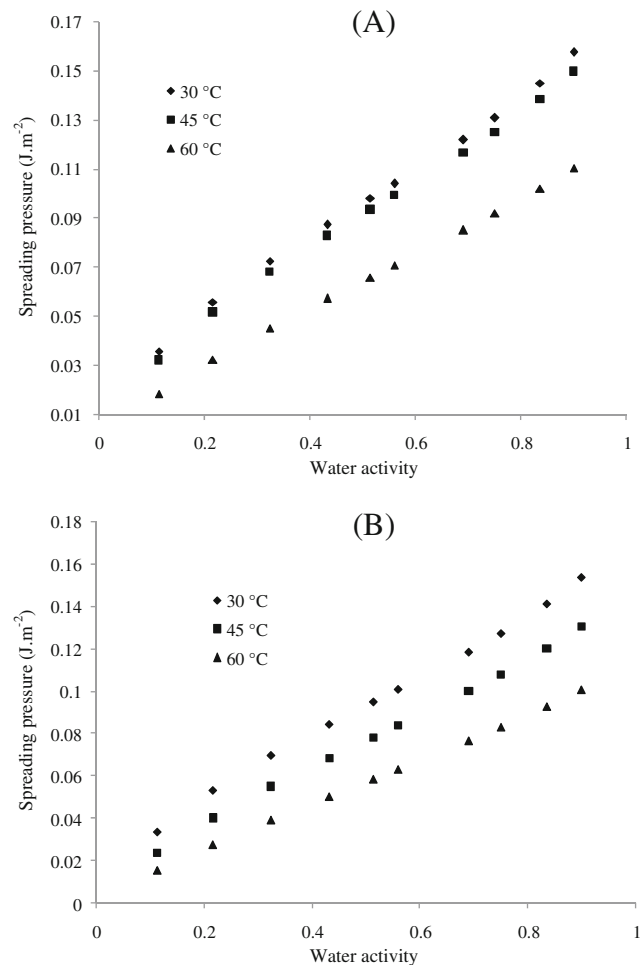Desorption: $q_{in} = 3695.98\, X_{eq}^{-0.595}$ with $r^2 = 0.993$

Fig. 4 Spreading pressure adsorption (**a**) and desorption (**b**) isotherms for cassava at different temperatures

Figure 2 shows the variation in the net integral entropy with equilibrium moisture content at 30 °C, for cassava. The net integral entropy of adsorption and desorption increased with increasing equilibrium moisture content. The net integral entropy values of adsorption are found to be greater than those for desorption at a constant equilibrium moisture content. As cassava adsorbed moisture, the entropy diminished to a minimum point that is considered as that of maximum stability, because it is where the water molecules achieve a more ordered arrangement within the solid. The minimum integral entropy value found at 30 °C was 0.154 kg water/kg db for cassava. The minimum entropy can be interpreted as the monolayer moisture content. This minimum value was

Table 7 Characteristic parameters for q_{st} versus ΔS relationship

	T_β (K)	ΔG_β (kJ.mol^{-1})	r^2
Adsorption	366.3	−1.172	0.999
Desorption	364	−1.221	0.999

Table 8 Maximum stability condition of cassava

T (°C)	X_{eq} (kg water/kg db)	a_w
30	0.154	0.619
45	0.107	0.640
60	0.053	0.580

expected to arise where strong bonding occurs between adsorbent and adsorbate which corresponds to less water being available for spoilage reactions. It can also be seen from Fig. 2 that the equilibrium moisture content corresponding to the minimum integral entropy value for cassava to achieve maximum stability was greater than corresponding to the GAB monolayer. The conditions for maximum storage stability of the cassava were shown in Table 8. As can be appreciated, as temperature increases the water activity decreases.

For all of the equilibrium moisture content range the net integral entropy values were negative. Negative net integral entropy values were attributed to the existence of chemical adsorption and/or structural modifications of the absorbent (Iglesias et al. 1976). The net integral entropy data conform to a power law relation as represented by the equation:

Adsorption: $\Delta S_{in} = -14.85\,X_{eq}^{-0.412}$ with $r^2{=}0.978$
Desorption: $\Delta S_{in} = -16.26\,X_{eq}^{-0.439}$ with $r^2{=}0.981$

The thermodynamic analysis of moisture sorption in dried foodstuffs has drawn interest because it provides a more thorough interpretation of the sorption isotherm phenomenon and helps to understood better the sorption mechanism (Beristain et al. 2002). Thermodynamic parameters such as net isosteric heat, differential entropy, net integral enthalpy and entropy could be used to determine interactions of water and food substances and to provide information useful for assessing food processing operations such as drying, mixing and storage. These parameters also improve the design of the food drying process, for instance establishing the drying conditions, to fix the end-point of the process or the determination of the energy requirements.

Conclusion

In this study, the sorption isotherms of cassava were determined at the temperatures of 30, 45 and 60 °C over the water activity range of 0.10 to 0.90, using the static gravimetric method. The sorption isotherms of cassava presented a sigmoidal shape. Equilibrium moisture contents were found to decrease with increasing temperature at constant water activity. They were also found to increase with increasing water activity at a given temperature. Hysteresis is evident over the entire range of water activity. All models presented a good fit to the experimental data. However, the GAB model described well the sorption isotherms of cassava.

On the basis of the thermodynamic analysis the following conclusions can be also drawn:

– The net isosteric heats of adsorption and desorption decreased with increasing equilibrium moisture content. The net isosteric heat is higher for desorption than adsorption at a constant equilibrium moisture content

indicating that the desorption process involves more energy than adsorption.
– The differential entropy of cassava decreased with increasing equilibrium moisture content.
– The net isosteric heats versus differential entropy data satisfy the enthalpy-entropy compensation theory.
– Net integral enthalpy of adsorption and desorption decreased with increasing equilibrium moisture content. In a reverse manner, net integral entropy increased with increasing equilibrium moisture content. The minimum integral entropy was proposed as indicative of the most suitable conditions for storage, with the corresponding water activity being available from the isotherm; this is in the range of 0.580–0.691 for the temperature range between 30 and 60 °C.

All thermodynamic functions such as net isosteric heat, differential entropy, net integral enthalpy and entropy were adequately characterised by a power law model.

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