

Effect of moisture sorption hysteresis on thermodynamic properties of two millet varieties

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Abstract: Application of reversible thermodynamic principles to gain fundamental understanding of food–water interactions in foods has met with limited success due to the presence of moisture sorption hysteresis which is a manifestation of irreversibility. This study was aimed at understanding the nature and extent of influence of hysteresis on thermodynamic properties of two millet varieties namely EX-BORNO and SOSAT C88. Moisture sorption data (adsorption and desorption) in the water activity and temperature ranges of 0.07 – 0.98 and 30 °C – 70 °C, respectively were used. Ratio of latent heat of moisture sorption to the latent heat of pure water was determined using Clausius-Clapeyron equation. Effect of moisture content on ratio of latent heat of sorption to latent heat of pure water was determined using Gallaher model. Net integral enthalpy was determined at constant spreading pressure with monolayer moisture contents calculated using Brunauer-Emmett-Teller (BET) and Guggenheim-Anderson-de Boer (GAB) models. Spreading pressure was determined using an analytical procedure. Gibbs equation was used to evaluate net integral entropy. Net isosteric heat of sorption and differential entropy were evaluated and used to investigate the enthalpy - entropy compensation theory. Latent heat of moisture sorption in the two millet varieties decreased with increase in moisture content and approached latent heat of pure water at a 'free water' point of between 32% and 42% moisture content (d.b.) in adsorption and desorption, respectively. Desorption latent heat of moisture was higher than the adsorption values and the difference decreased with increase in moisture content. Monolayer moisture content decreased with increase in temperature, with the GAB being higher than the BET values. Desorption monolayer moisture was higher than that of adsorption. Spreading pressure increased with increase in water activity, with adsorption isotherm being higher than that of desorption and temperature having no significant effect. Net integral enthalpy decreased with increase in moisture content with effect of hysteresis being more marked in EX-BORNO than in SOSAT C88. Net integral entropy decreased with increase in moisture content to minimum values and thereafter, maintained sinusoidal trend with adsorption curve lagging behind desorption and varnishing at 18% and 16% (db) moisture content in EX-BORNO and SOSAT C88 respectively. Net isosteric heat of sorption and differential entropy decreased with increase in moisture content with effect of hysteresis being more pronounced in EX-BORNO. Moisture sorption process in the grains was found to be enthalpy driven with differential enthalpy varying linearly with differential entropy. Inequality in isokinetic and harmonic mean temperatures confirmed the enthalpy - entropy compensation theory. Hysteresis was found to have effect on the isokinetic temperature, causing the values of desorption isokinetic temperature to be higher than the adsorption values.

Keywords: EX-BORNO, SOSAT C88, latent heat of moisture sorption, spreading pressure, net integral enthalpy and entropy, isosteric heat, differential entropy, enthalpy-entropy compensation

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1 Introduction

Millets are a group of highly variable small-seeded grasses, widely grown around the world as cereal crops or grains for both human food and livestock

fodder. Millets are important crops in the semi-arid tropics of Asia and Africa (especially in India, Nigeria, and Niger), with 97% of world millet production taking place in developing countries (McDonough et al. 2000). The crop is grown extensively in the northern part of Nigeria. It is an early maturing crop that tolerates drought much better than most other cereals like maize and sorghum. There are two major local varieties of millet

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available namely EX-BORNO with a yield potential of 2000–3000 kg/ha and SOSAT C88 with a yield potential of 2500–3500 kg/ha (LCRI, 1997). The grains are consumed locally as *tuwo* (porridge produced from ground wet mash), *fura* (refreshing drink), *koko* (pap food drink made from dried flour or wet mash) and many other forms depending on local dietary habits (Ikwelle et al., 1993). There are technological possibilities of the utilization of millet in such industrial applications as starch production (Nkama, 1998). Drying is a fundamental operation in the processing of millet grains. The most common drying method for this crop in the tropics is the open-air-sun-drying. However, this drying technique is slow, uncontrolled, exposed to environmental contamination and requires hard labor. Furthermore, direct exposure to solar radiation may affect the quality of the dried product significantly. The large scale production of millet and the wide range of possible products from it will require that the open-air-sun-drying method currently practiced be replaced with efficient drying systems.

Thermodynamics has been reported as one of the three approaches used to understand the properties of water and calculate the energy requirements of heat and mass transfer in biological systems (Fasina et al., 1999; Rizvi, 1986). Others include the structural approach, which describes the mechanism of hydrogen bonding and molecular positioning obtained using spectroscopic techniques, and the dynamic approach, which involves the analysis of motion of water molecules and their contribution to the hydrodynamic properties of the system. Thermodynamic properties of food relate the concentration of water in the material to its partial pressure, which is crucial in the analysis of heat and mass transport phenomena during drying. They determine the end point to which food must be dehydrated in order to achieve a stable product with optimal moisture content, and yield a figure for the theoretical minimum amount of energy required to remove a given amount of water from food. The properties also provide insight into the microstructure associated with the food–water interface (Rizvi, 1986).

Thermodynamic functions are readily calculated from moisture sorption isotherms and this enables the thermodynamic approach to allow the interpretation of experimental results in accordance with the statement of the theory (Iglesias and Chirife, 1976a). The functions include free energy, differential heat of sorption, integral enthalpy and integral entropy. Enthalpy represents the total energy available to do work, while entropy at any temperature provides lost work and gives a measure of the energy that is not available to perform work. Thus, the energy that is available to do work is the difference between these two quantities. This is known as Gibbs free energy. This free energy, also known as heat of vaporization, is therefore, the total energy required to transfer water molecules from the vapor state to the solid surface and vice versa. It is a measure of work done by the system to accomplish an adsorption or desorption process, and can be used as an indicator of the state of adsorbed water by solid particles (Fasina et al., 1999). The state of adsorbed water is a measure of the physical, chemical and microbial stability of biological materials under storage (Labuza, 1968). Heat of vaporization is also useful in evaluating drying models, determining energy consumption during the drying and wetting of food products, designing the drying equipment and describing the heat and mass transfer related processes. In a multi-component system such as food, some considerations have to be given to the composition, and Gibbs free energy will depend not only on temperature and pressure, but also on the amount of each component present in the system. The moisture sorption isotherms at different temperatures can be used to evaluate the heat of sorption, which determines the interaction between an adsorbent and adsorbate. They also provide information on hydration energy requirement, food microstructure, physical phenomena on the food surfaces, water properties and sorption kinetic parameters (Arslan and Toğrul, 2006; McMinn and Magee, 2003).

Enthalpy–entropy compensation theory is used to evaluate physical and chemical phenomena such as

sorption reactions. The theory states that in order to minimize free energy changes due to these phenomena, compensation arises from the nature of the interaction between the solute and solvent causing the reaction in such a way that the relationship between the enthalpy and entropy for the specific reaction remain linear (Fasina, 2006; Koumoutsakos and Avramidis, 1999). Enthalpy change provides a measure of the energy variations occurring on mixing water molecules with sorbent during sorption process. Entropy defines the degree of order or randomness existing in the water-sorbent system and helps in the interpretation of such processes as dissolution, crystallization and swelling (McMinn et al., 2005). The enthalpy–entropy compensation theory has been investigated for many different physical and chemical processes (Aguerre et al., 1986; Madamba et al., 1996; Telis et al., 2000).

Moisture sorption hysteresis is the phenomenon by which two different paths exist between the adsorption and desorption isotherms. It has been stated that the extent of hysteresis is related to the nature and state of the components in a food, reflecting their potential for structural and conformational rearrangements, which alter the accessibility of energetically favourable polar sites (Kapsalis, 1981).

The main objectives of this study were to 1) evaluate the ability of five commonly used moisture sorption isotherm models to express water activity as a function of moisture content in the EX-BORNO and SOSAT C88 millet varieties, 2) determine the influence of hysteresis on such thermodynamic properties as monolayer moisture content, heat of moisture sorption, spreading pressure of moisture, net integral enthalpy, net integral entropy, net isosteric heat of sorption, and differential entropy for the two millet varieties, using the moisture desorption and adsorption data, and 3) verify the applicability of enthalpy–entropy compensation theory to the adsorption and desorption phenomena in EX-BORNO and SOSAT C88 millet grains.

2 Materials and methods

2.1 Materials

The grains of EX-BORNO and SOSAT C88 millet varieties used in the study were obtained from Lake Chad Research Institute (LCRI), Maiduguri in Borno State, Nigeria. Sample preparation and initial moisture content determination procedures for the grains subjected to the adsorption and desorption processes have been respectively presented in Raji and Ojediran (2011).

2.2 Methods

The static gravimetric method involving the use of saturated salt solutions in the temperature and water activity ranges of 30-70°C and 0.07-0.97, respectively was used to obtain the adsorption and desorption equilibrium moisture content-water activity data of the two millet varieties (Raji and Ojediran, 2011).

2.3 Data and analysis

The adsorption and desorption equilibrium moisture content – water activity data at different temperatures used in carrying out analysis and investigating the effect of hysteresis on moisture sorption thermodynamic properties of EX-BORNO and SOSAT C88 millet varieties, obtained from Raji and Ojediran (2011), are presented in Tables 1 and 2. Values of water activity used in thermodynamic analysis at different temperatures were obtained by fitting the equilibrium moisture content – water activity data of the grains to the water activity version of five commonly used moisture sorption isotherm models (Table 3) and determining the model that best described their water activity – equilibrium moisture relationships. The non-linear regression procedure in SPSS 20.0 for Windows as employed by Aviara et al. (2004) was used to solve the models for water activity as a function of equilibrium moisture content. The predictive performance of the models was measured using coefficient of determination, (R^2) and standard error of estimate (SE). A model was considered better than another if it had a lower standard error and higher R^2 .

Table 1 Adsorption (Ads) and desorption (Des) equilibrium moisture contents (EMC) of EX-BORNO millet at five temperatures and different water activities (a_w)

30 °C	a_w	0.07	0.11	0.22	0.32	0.51	0.55	0.70	0.80	0.92	0.97
	Ads EMC	14.4	17.1	22.0	23.3	23.8	24.0	25.7	27.0	31.6	35.3
	Des EMC	14.4	17.1	22.0	24.2	25.6	26.0	26.5	27.0	31.6	35.3
40 °C	a_w	0.07	0.11	0.22	0.32	0.51	0.61	0.71	0.82	0.89	0.98
	Ads EMC	12.8	15.5	19.7	20.8	21.3	21.8	22.7	24.7	27.0	31.1
	Des EMC	12.8	15.5	19.7	22.1	22.9	23.3	23.9	24.7	27.4	31.1
50 °C	a_w	0.07	0.11	0.21	0.31	0.50	0.60	0.70	0.81	0.89	0.96
	Ads EMC	10.0	13.4	17.2	17.8	18.2	19.0	19.7	21.5	24.5	27.3
	Des EMC	10.0	13.5	17.2	18.6	19.7	20.1	20.6	21.5	24.6	27.3
60 °C	a_w	0.07	0.11	0.21	0.31	0.50	0.60	0.70	0.80	0.88	0.95
	Ads EMC	8.5	11.5	14.0	14.2	14.7	15.0	15.7	18.5	21.4	25.0
	Des EMC	8.5	11.5	15.9	16.9	17.0	17.1	17.5	18.7	21.5	25.0
70 °C	a_w	0.07	0.11	0.20	0.30	0.50	0.60	0.70	0.80	0.88	0.94
	Ads EMC	7.0	10.0	11.5	11.9	12.3	12.7	13.9	16.1	19.2	22.3
	Des EMC	7.0	10.0	12.9	14.0	14.6	15.0	15.5	16.4	19.3	22.3

Table 2 Adsorption(Ads) and desorption (Des) equilibrium moisture contents (EMC) of SOSAT C88 millet at five temperatures and different water activities (a_w)

30 °C	a_w	0.07	0.11	0.22	0.32	0.51	0.55	0.70	0.80	0.92	0.97
	Ads EMC	10.4	13.6	16.3	17.3	19.1	19.3	21.0	23.0	27.7	32.0
	Des EMC	10.4	13.6	16.3	18.0	19.8	20.1	21.7	23.8	27.7	32.0
40 °C	a_w	0.07	0.11	0.22	0.32	0.51	0.61	0.71	0.82	0.89	0.98
	Ads EMC	8.3	11.5	14.4	15.4	16.8	17.4	19.0	21.5	23.5	27.9
	Des EMC	8.3	11.5	14.4	15.9	17.7	18.8	20.2	22.0	23.5	27.9
50 °C	a_w	0.07	0.11	0.21	0.31	0.50	0.60	0.70	0.81	0.89	0.96
	Ads EMC	7.9	10.4	12.0	13.1	14.0	15.2	17.3	20.0	22.9	25.8
	Des EMC	8.0	10.5	13.0	14.9	16.1	17.0	18.2	20.3	22.9	25.8
60 °C	a_w	0.07	0.11	0.21	0.31	0.50	0.60	0.70	0.80	0.88	0.95
	Ads EMC	7.5	9.4	10.5	11.0	12.3	13.5	15.1	17.5	20.5	23.2
	Des EMC	7.5	9.4	11.5	12.7	13.9	14.7	16.0	18.0	20.5	23.2
70 °C	a_w	0.07	0.11	0.20	0.30	0.50	0.60	0.70	0.80	0.88	0.94
	Ads EMC	6.0	8.4	9.2	9.6	10.9	11.9	13.2	15.3	18.7	21.2
	Des EMC	6.0	8.4	10.5	11.6	13.1	14.0	15.0	16.6	18.7	21.2

Source: Raji and Ojediran (2011)

2.4 Determination of thermodynamic properties

2.4.1 Latent heat of moisture sorption (L)

The latent heat of moisture sorption in the grains was estimated by applying the Clausius-Clapeyron equation to the sorption isotherms. The Clausius-Clapeyron equation (Kapsalis, 1987; Fasina et al., 1999) after some

mathematical manipulations (Aviara and Ajibola, 2000) yields:

$$\ln(P_o) = \frac{L}{h_{fg}} \ln(P_s) + C \quad (1)$$

Where: C is a constant, P_s is the saturation vapor pressure, P_o vapor pressure of moisture in material. A plot

of $\ln(P_o)$ versus $\ln(P_s)$ yields the ratio of the latent heat of moisture in the material to the latent heat of saturated water vapour from the slope of the straight line obtained.

The saturation vapor pressure (P_s) at different temperatures was obtained either from Rogers and

Mayhew (1981) or calculated using the psychrometric relationships in ASAE (1996). The vapor pressure in the material (P_o) was determined using the equation:

$$P_o = a_w P_s \tag{2}$$

Table 3 Five commonly used moisture sorption isotherm models

Name of model	Equilibrium moisture content model	Water activity model
Modified Oswin (Chen and Morey, 1989)	$M = (A + BT) \left[\frac{a_w}{1 - a_w} \right]^{1/c}$	$a_w = \frac{1}{\left[\frac{A+BT}{M} \right]^c + 1}$
Modified Halsey (Iglesias and Chirife, 1976a)	$M = \left[\frac{-\ln(a_w)}{\exp(A + BT)} \right]^{-1/c}$	$a_w = \exp[-\exp(A + BT) M^{-c}]$
Modified Chung-Pfost (Pfost et al., 1976)	$M = \frac{-1}{C} \ln \left[\left[\frac{-(T + B)}{A} \right] \ln(a_w) \right]$	$a_w = \exp \left[\left[\frac{-A}{(T + B)} \right] \exp(-CM) \right]$
Modified Henderson (Thompson, 1972)	$M = \left[\frac{-\ln(1 - a_w)}{A(T + B)} \right]^{1/c}$	$a_w = 1 - \exp[-A(T + B)M^c]$
Modified Hailwood and Horrobin (Aviara and Igbeka, 2015)	$M = \left[T \left(\frac{A}{a_w} + B \right) - \frac{Ca_w}{T^6} \right]^{-1}$	$a_w = \frac{-\left(\frac{1}{M} - BT\right) \pm \left[\left(\frac{1}{M} - BT\right)^2 + \frac{4CA}{T^6} \right]^{1/2}}{\frac{2C}{T^6}}$

Note: M , moisture content, % (d.b.); a_w , water activity (decimal); T , absolute temperature, K ; A , B and C , constants specific to individual equations.

The model that best described the EMC- a_w relations of EX-BORNO and SOSAT C88 millet grains was used to determine the water activity values.

Water activity values were obtained at five temperatures of 30, 40, 50, 60 and 70°C and four moisture levels in the range of 11%-22%. The natural log of actual vapour pressure [$\ln(P_o)$] was plotted against the natural log of saturated water vapour pressure [$\ln(P_s)$] at the same temperature. $\ln(P_o)$ was regressed against $\ln(P_s)$ to establish the linear relationship existing between them. The ratios of the heat of moisture sorption in the grains to the latent heat of saturated water vapour at different moisture contents were determined from the slopes of the straight lines obtained. The non-linear regression procedure in SPSS 20 for Windows was then used to fit the Gallaher model (Aviara et al., 2004) to the data obtained on the heat of moisture sorption ratios. This equation relates the moisture content of food and agricultural material to the ratio of the heat of moisture sorption in the product (L) to the latent heat of saturated water vapour (h_{fg}) and can be stated as follows:

$$\frac{L}{h_{fg}} = 1 + a \exp(-bM) \tag{3}$$

The values of coefficients a and b were obtained by logarithmic transformation of Equation (3) to yield Equation (4):

$$\ln \left(\frac{L}{h_{fg}} - 1 \right) = -bM + \ln a \tag{4}$$

A plot of $\ln \left(\frac{L}{h_{fg}} - 1 \right)$ against M was used to determine the initial values of a and b from the slope of the straight line obtained. The values of coefficients a and b obtained from non-linear regression were used to compute the values of $\frac{L}{h_{fg}}$ and plotted against moisture content.

2.4.2 Monolayer moisture content (M_m)

Monolayer moisture is a limiting value at which the rate of quality loss in biological materials is negligible (Bell and Labuza, 2000). It is a crucial parameter in the determination of the surface potential of moisture sorbed in food. Two moisture sorption isotherm models that are normally used to determine the monolayer moisture content of foods were tested for EX-BORNO and SOSAT C88 millet grains. These models are:

- a. Brunauer-Emmett-Teller (BET) Model

The BET equation, which is the most widely used model in food systems, was first proposed by Brunauer et al. (1938). The BET equation can be stated as:

$$M = \frac{M_m C a_w}{(1-a_w)(C a_w - a_w + 1)} \quad (5)$$

After some algebraic manipulations (Menkov, 2000), Equation (5) became linearised to yield the following Equation

$$\frac{a_w}{(1-a_w)M} = \frac{1}{M_m C} + \frac{a_w(C-1)}{M_m C} \quad (6)$$

Where: M_m is the monolayer moisture content, which represents the moisture content at which the water attached to each polar and ionic groups starts to behave as a liquid-like phase, a_w is the water activity, M is the equilibrium moisture content and, C is the energy constant related to the net heat of sorption. Since the standard BET equation does not involve the temperature effect, the monolayer moisture content was calculated separately for each temperature. The plot of $a_w/[M(1 - a_w)]$ versus a_w was used to determine the BET monolayer moisture content and constant C from the straight line obtained for each temperature at $a_w < 0.45$. Values of M_m obtained were plotted against temperature.

b. Guggenheim-Anderson-de Boer (GAB) Model

The GAB (Guggenheim, Anderson and De Boer) model was derived from a refinement of the Langmuir and BET theories of physical adsorption (Van den Berg, 1984). It can be expressed as:

$$M = \frac{CkM_m a_w}{(a - k a_w)(1 - k a_w + C k a_w)} \quad (7)$$

where: M_m is the monolayer moisture content; C and k are the adsorption constants. Equation (7) was transformed into a polynomial of the second order (Equation 8) and used to determine its constants and the monolayer moisture content.

$$\frac{a_w}{M} = \partial a_w^2 + b a_w + C \quad (8)$$

Where: $\partial = \frac{k}{M_m} \left(\frac{1}{C} - 1 \right)$, $b = \frac{1}{M_m} \left(1 - \frac{2}{C} \right)$, and

$$C = \frac{1}{M_m C k}$$

Equation (8) was solved by plotting $\frac{a_w}{M}$ vs a_w for both adsorption and desorption in EX-BORNO and SOSAT C88 millet at each temperature and fitting the plot with a second order polynomial. The M_m values obtained were then plotted against temperature.

2.4.3 Spreading pressure

Spreading pressure was estimated using an analytical procedure similar to the one described by Iglesias et al. (1976) and Fasina et al. (1999) from the relationship:

$$\phi = \frac{KT}{A_m} \int_0^{a_w} \frac{\theta}{a_w} da_w \quad (9)$$

$$\theta = \frac{M}{M_m} \quad (10)$$

Where: ϕ is the spreading pressure (Jm^{-2}), K is the Boltzman constant ($1.380 \times 10^{-23} \text{ J K}^{-1}$), and A_m is the surface area of a water molecule ($1.06 \times 10^{-19} \text{ m}^2$).

The monolayer moisture contents (M_m) of the product used were the BET values. Equation (9) becomes indeterminate at $a_w = 0.0$, therefore, the lower limit of water activity employed was 0.05. Computed value of spreading pressure was adjusted by adding the value corresponding to the water activity interval of 0.0-0.05 which was evaluated by assuming a linear relationship (Henry's law) between a_w and θ (Fasina et al., 1999). In the water activity range of 0.0-0.05, Equation (9) becomes

$$\phi = \frac{KTM}{A_m M_m} \quad (11)$$

Spreading pressure values were plotted against water activity at different temperatures to obtain the spreading pressure isotherms.

2.4.4 Net integral enthalpy

Net integral enthalpy was evaluated at constant spreading pressure using the following Equation:

$$\left[\frac{d(\ln a_w)}{d(1/T)} \right]_{\phi} = \frac{-Q_{in}}{R} \quad (12)$$

Where: Q_{in} is the integral enthalpy (J/kg), T is the absolute temperature (K), a_w is the water activity, R is the

gas constant of water vapour (J/kg^1) and ϕ is the spreading pressure (J/m^2).

A plot of $\ln(a_w)$ versus $1/T$ at constant spreading pressure yielded the net integral enthalpy from the slope of the straight line obtained. Values of integral enthalpy obtained were plotted against moisture content.

2.4.5 Net integral entropy

Net integral entropy was evaluated using the following relationship (Benado and Rizvi, 1985):

$$S_{in} = \frac{-Q_{in}}{T} - R \ln a_w^* \quad (13)$$

Where: S_{in} is the net integral entropy ($J \text{ kg}^{-1} \text{ K}^{-1}$), and a_w^* is the geometric mean water activity obtained at constant spreading pressure. The temperature term of Equation (13) was interpolated linearly for a_w^* from the T and a_w data for a given ϕ using the approach of Igathinathane et al. (2007).

2.4.6 Net isosteric heat of sorption

Isosteric heat of sorption (kJ/mol), is defined as the heat of sorption at constant specific volume, evaluated using the Clausius-Clapeyron equation at constant moisture content, and is a measure of moisture-solid site binding strength. Net isosteric heat of sorption was determined using the Clausius-Clapeyron equation that relates water activity and temperature at a constant moisture content (Rizvi, 1986; Bell and Labuza, 2000):

$$\frac{d(\ln a_w)}{d(1/T)} = -\frac{q_{st}}{R} \quad (14)$$

Where: T is the absolute temperature (K), q_{st} is the net isosteric heat of sorption (kJ/mol), and R is the universal gas constant ($8.31434 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$). The required a_w values at specified moisture content for various temperatures were calculated using the moisture sorption isotherm model that best described the moisture sorption data of the grains. The net isosteric heat sorption was obtained as the slope of the plot of $\ln(a_w)$ versus $1/T$ at different moisture content values. Adding latent heat of pure water to the net isosteric heat of sorption gave the isosteric heat of sorption (Q_{st}), which is also known as differential enthalpy.

The isosteric heat of sorption (Q_{st}) (kJ/mol) was obtained using Equation 15

$$Q_{st} = q_{st} + L_v \quad (15)$$

Where: L_v is the latent heat of pure water (44.045 kJ/mol at 25°C).

2.4.7 Differential entropy

By substituting the Gibbs free energy in the Gibbs-Helmholtz equation (McMinn and Magee, 2003; Kaya and Kahyaoglu, 2005), the differential entropy was calculated using the following Equation:

$$-\ln a_w|_M = \frac{-Q_{st}}{RT} + \frac{S_d}{R} \quad (16)$$

Where: S_d is the differential entropy of sorption ($kJ \text{ mol}^{-1} \text{ K}^{-1}$), $\ln(a_w)$ versus $1/T$ for different constant moisture contents was plotted, and the S_d was obtained from the intercept on the y-axis.

2.4.8 Enthalpy - entropy compensation theory

A linear relationship between the isosteric heat of sorption (differential enthalpy) and differential entropy was used to establish the enthalpy-entropy compensation theory (McMinn and Magee, 2003; Arslan and Toğrul, 2006) as follows:

$$Q_{st} = T_\beta S_d + \alpha \quad (17)$$

Where: Q_{st} is the isosteric heat of sorption (kJ/mol), T_β is the isokinetic temperature (K), and α is a constant.

The isokinetic temperature (T_β) which indicates the temperature, at which all reactions in the series proceed at the same rate, is also the characteristic property of the material surface (Aguerre et al., 1986). It is represented by the slope of the enthalpy-entropy linear relationship. The free energy (G_β) at T_β , provides a criterion for determining whether water sorption is a spontaneous ($-G_\beta$) or nonspontaneous ($+G_\beta$) process. To test the validity of the compensation theory, the isokinetic temperature was compared with the harmonic mean temperature (T_{hm}) given by Equation (18).

$$T_{hm} = \frac{n}{\sum_{i=1}^n (1/T_i)} \quad (18)$$

Linear enthalpy-entropy compensation theory applies only when $T_\beta \neq T_{hm}$ and the process is said to be enthalpy

driven if $T_{\beta} > T_{hm}$ or entropy driven if $T_{\beta} < T_{hm}$ (McMinn et al., 2005). Equation (18) shows that T_{hm} is a function of temperature levels (T) selected for the experiment and is independent of the material considered.

3 Results and discussion

3.1 Selection of water activity model

The parameters estimates of the water activity (a_w) models for both EX-BORNO and SOSAT C88 in adsorption and desorption respectively are shown in Tables 4 and 5. The Tables show the values of the indices used in comparing the models namely the coefficient of determination and standard error. Several investigators reported similar tables in literature (Duggal et al., 1982; Ajibola and Adams, 1986, Aviara et al., 2002, Aviara et al., 2004). Out of the five water activity models tested, the modified Oswin model, which gave the least standard error and highest coefficient of determination, was considered the best model for predicting the water activity of the grains. This was followed closely by the modified Halsey and modified Chung–Pfof models. The modified Oswin model became the moisture sorption isotherm

equation that was used in determining the water activity for thermodynamic analysis of EX-BORNO and SOSAT C88 millet in both adsorption and desorption processes.

In terms a_w as a function of EMC, the following Equations are the Modified Oswin model expressions for the grains.

EX-BORNO:

Adsorption:

$$a_w = \frac{1}{\left[\frac{112.66-0.292T}{M_a}\right]^{9.912} + 1} \tag{19}$$

Desorption:

$$a_w = \frac{1}{\left[\frac{104.92-0.264T}{M_d}\right]^{12.43} + 1} \tag{20}$$

SOSAT C88:

Adsorption:

$$a_w = \frac{1}{\left[\frac{75.75-0.188T}{M_a}\right]^{5.824} + 1} \tag{21}$$

Desorption:

$$a_w = \frac{1}{\left[\frac{67.58-0.159T}{M_d}\right]^{6.184} + 1} \tag{22}$$

Table 4 Estimated parameters and comparison for the water activity model of EX-BORNO millet

Parameter and criteria	Water activity models									
	Adsorption					Desorption				
	Modified Oswin	Modified Halsey	Modified Chung and Pfof	Modified Henderson	Modified Hailwood and Horrobin	Modified Oswin	Modified Halsey	Modified Chung and Pfof	Modified Henderson	Modified Hailwood and Horrobin
A	112.66	56.985	650.734	-5.184E-9	9.411E-6	104.918	62.984	1134.57	-4.286E-9	-4.849E-5
B	-0.292	-0.115	-297.39	-249493	0	-0.264	-0.117	-297.86	-155428	0
C	9.912	7.02	0.209	2.17	4.773E13	12.43	8.632	0.228	2.365	1.081E14
R ²	0.944	0.928	0.846	0.536	0.749	0.951	0.942	0.855	0.557	0.941
SE	0.519	0.817	0.846	1.49	1.10	0.485	0.736	0.835	1.46	0.533

Note: A, B, C are the models constants and R² is the value for the coefficient of determination SE is the standard error.

Table 5 Estimated parameters and comparison for the water activity model of SOSAT C88 millet

Parameter and criteria	Water activity models									
	Adsorption					Desorption				
	Modified Oswin	Modified Halsey	Modified Chung and Pfof	Modified Henderson	Modified Hailwood and Horrobin	Modified Oswin	Modified Halsey	Modified Chung and Pfof	Modified Henderson	Modified Hailwood and Horrobin
A	75.752	29.237	743.530	2.049E-6	3.817E-5	67.582	27.010	1094.96	-9.36E-10	-7.922E-5
B	-0.188	-0.057	-295.24	-292.632	0	-0.159	-0.046	-292.93	-226070	0
C	5.824	4.254	0.257	3.498	3.101E13	6.184	4.529	0.256	2.920	1.245E14
R ²	0.983	0.983	0.971	0.951	0.848	0.987	0.975	0.978	0.803	0.709
SE	0.29	0.28	0.37	0.48	0.855	0.25	0.35	0.33	0.62	1.18

Note: A, B, C are the models constants, R² is the value for the coefficient of determination and SE is the standard error.

3.2 Latent heat of moisture sorption (L)

Figure 1 shows the plot of $\ln(P_o)$ vs $\ln(P_s)$ for EX-BORNO and SOSAT C88 millet respectively, at different moisture contents for adsorption and desorption. The natural log of the actual vapour pressure ($\ln(P_o)$) increased linearly with increase in the natural log of saturated water vapour pressure ($\ln(P_s)$) and moisture content. The relationships existing between the $\ln(P_o)$ and $\ln(P_s)$ of the two millet varieties at different moisture contents are represented by the following Equations:

EX-BORNO at 15, 17, 20 and 22% moisture content,

In adsorption

$$\ln(P_o) = 3.3145\ln(P_s) - 23.962 \quad (23)$$

$$\ln(P_o) = 2.8119\ln(P_s) - 18.485 \quad (24)$$

$$\ln(P_o) = 2.0162\ln(P_s) - 10.238 \quad (25)$$

$$\ln(P_o) = 1.6184\ln(P_s) - 6.2048 \quad (26)$$

In desorption

$$\ln(P_o) = 3.935\ln(P_s) - 30.908 \quad (27)$$

$$\ln(P_o) = 3.3936\ln(P_s) - 24.644 \quad (28)$$

$$\ln(P_o) = 2.4177\ln(P_s) - 14.328 \quad (29)$$

$$\ln(P_o) = 1.8564\ln(P_s) - 8.5959 \quad (30)$$

The coefficients of determination (R^2) were 0.997, 0.987, 0.973, 0.974, 0.997, 0.997, 0.973 and 0.966 respectively.

SOSAT C88 at 11, 15, 18 and 21% moisture content,

In adsorption

$$\ln(P_o) = 2.2083\ln(P_s) - 13.307 \quad (31)$$

$$\ln(P_o) = 1.6979\ln(P_s) - 7.3382 \quad (32)$$

$$\ln(P_o) = 1.3796\ln(P_s) - 3.9373 \quad (33)$$

$$\ln(P_o) = 1.1964\ln(P_s) - 2.0215 \quad (34)$$

In desorption

$$\ln(P_o) = 2.099\ln(P_s) - 12.783 \quad (35)$$

$$\ln(P_o) = 1.7225\ln(P_s) - 7.7977 \quad (36)$$

$$\ln(P_o) = 1.4149\ln(P_s) - 4.3784 \quad (37)$$

$$\ln(P_o) = 1.216\ln(P_s) - 2.2532 \quad (38)$$

with coefficients of determination (R^2) being 0.9994, 0.9986, 0.9975, 0.9984, 0.9987, 0.9997, 0.9987 and 0.9991, respectively.

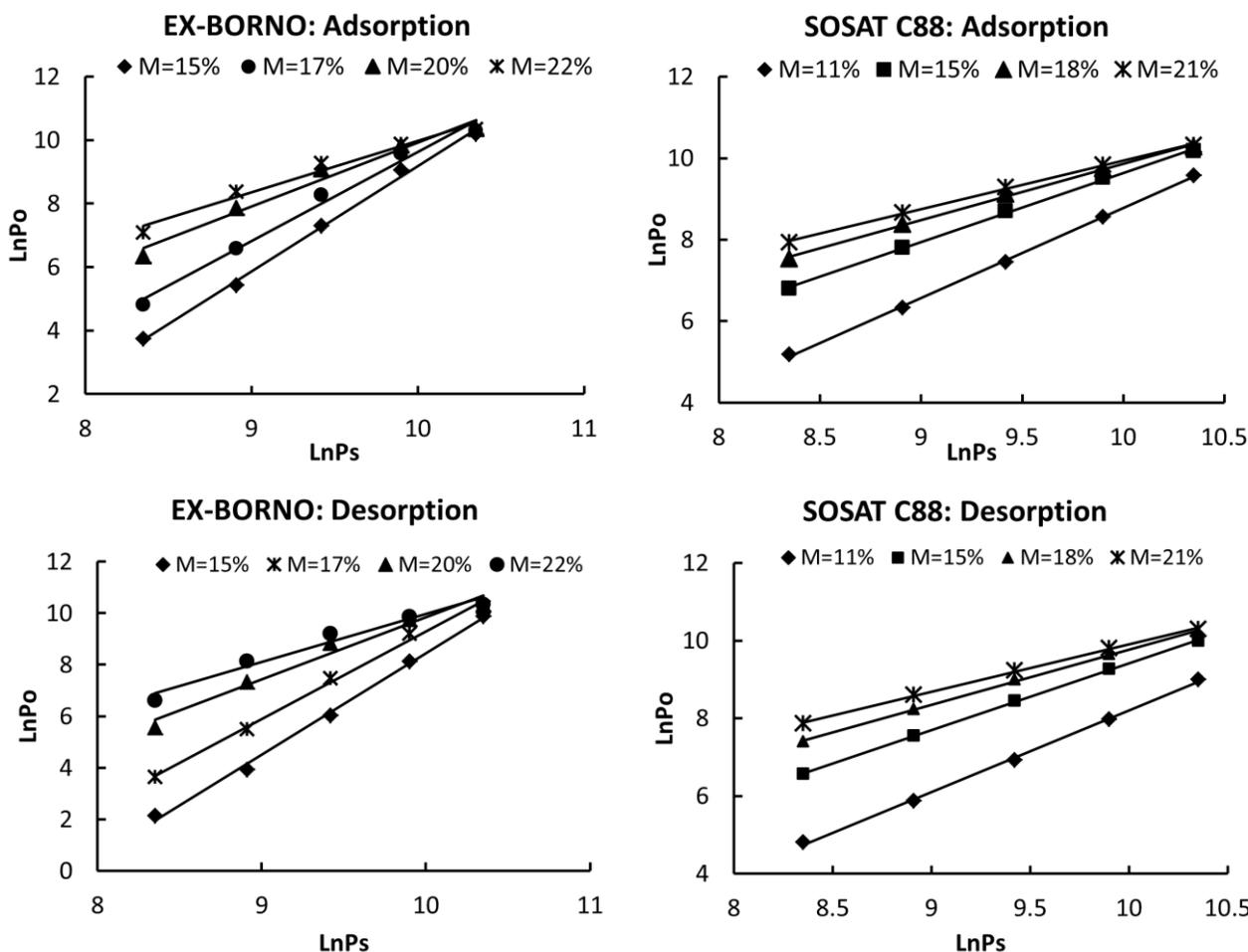


Figure 1 Straight line relationships between $\ln(P_o)$ and $\ln(P_s)$ for EX-BORNO and SOSAT C88 millet grains (adsorption and desorption) at various moisture contents

Similar findings were reported for winged bean seed and gari (Fasina et al., 1999), unripe and ripe plantain (Aviara and Ajibola, 2000), melon seed and cassava (Aviara and Ajibola, 2002), sesame seed (Aviara et al., 2002), cowpea (Ajibola et al., 2003) and soya bean (Aviara et al., 2004). It was observed that the vapour pressure of water in the material (P_o) was higher during adsorption than during desorption. The shift toward higher relative vapor pressure during adsorption may have been caused by the activation energy required to open the unit layer stacks. The glass-rubber transition during adsorption and desorption might also have caused hysteresis due to the non-equilibrium state of phase transition. According to Kapsalis (1981), the contact angle of receding film in the Kelvin equation during desorption is smaller than that of the advancing film upon adsorption. This causes capillary condensation along the adsorption arm of the moisture sorption isotherm to be at a higher vapour pressure. Rahman (1999) noted that higher vapour pressure during adsorption is caused by the activation energy needed to open the unit layer stacks, while continual outflow of water from the material leads to reduction in vapour pressure during desorption. As a result of higher vapour pressure of water in the material during adsorption, the heat of moisture adsorption is lower compared to that of desorption. This is expected and clearly obvious, because during desorption, more energy is needed to convert the moisture in the material and on the material surface to another state (gas/vapour).

The existence of hysteresis in materials under sorption process makes accurate determination of the material's thermodynamic properties almost impossible, because it is very difficult to determine which arm of the isotherm (adsorption or desorption) represents true equilibrium condition under selected water activities.

The values of coefficients 'a' and 'b' in Equation (3) obtained for EX-BORNO were $a = 31.45$, $b = 17.211$ (adsorption) and $a = 32.254$, $b = 15.759$ (desorption), with their coefficients of determination as 0.98 and 0.98 respectively. For SOSAT C88 the coefficients were $a =$

7.3 , $b = 16.226$ (adsorption) and $a = 5.215$, $b = 13.944$ (desorption), with coefficients of determination as 0.99 and 0.98 respectively. Therefore Equation (3) becomes:

EX-BORNO

Adsorption:

$$\frac{L}{h_{fg}} = 1 + 31.45 \exp(-17.211M) \quad (39)$$

Desorption:

$$\frac{L}{h_{fg}} = 1 + 32.254 \exp(-15.759M) \quad (40)$$

SOSAT C88

Adsorption:

$$\frac{L}{h_{fg}} = 1 + 7.3 \exp(-16.226M) \quad (41)$$

Desorption:

$$\frac{L}{h_{fg}} = 1 + 5.215 \exp(-13.944M) \quad (42)$$

The above form of Equation has been used by many researchers to relate the free energy or latent heat of vaporization of agricultural crops to moisture content (Cenkowski et al., 1992, Aviara et al., 2004). The plots of the L/h_{fg} against moisture content for EX-BORNO and SOSAT C88 are shown in Figure 2. From this figure, it can be seen that the L/h_{fg} in EX-BORNO and SOSAT C88 decreased with increase in moisture content showing that at higher moisture levels, the strength of water binding decreased. The heat of moisture sorption in EX-BORNO approached the latent of pure water at the moisture content of about 38% in adsorption and 42% in desorption, while for SOSAT C88, it was at 32% in adsorption and 34% in desorption. The high moisture levels at which the 'free water point' (Aviara et al., 2002) occurred may be as a result of the hard nature of millet grains. Iglesias and Chirife (1976b) explained that the level of moisture content at which the heat of sorption (L) approaches the heat of vaporization of water can be sign of water existing in free form in food products. Similar findings were reported by Aviara et al. (2004) on soybean, Aviara et al. (2002) on sesame seed, Aviara and Ajibola (2002) on melon seed and cassava, and Fasina et al. (1999) on winged bean seed and gari.

From Figure 2, it can be seen that the effect of hysteresis on latent heat of moisture sorption in the grains (heat of desorption being higher than that of adsorption), decreased with increase in moisture content and completely disappeared at higher moisture levels. This shows that at higher moisture levels, water in the material is loosely held by cohesive forces, and this implies that less and almost equal amount of energy is would be needed in both desorption and adsorption to remove water from the material or cause the material to absorb moisture. As the moisture content decreases, the adhesion and cohesion between water and material components

increases (Iglesias and Chirife, 1976c, Al-Mutaseb et al., 2004), hence more energy becomes needed to move the water molecules (Wang and Brennan, 1991, Vega-Galvez et al., 2008). The higher values of heat of desorption over that of adsorption at lower moisture levels indicates that the energy required for water desorption process was higher than that needed for moisture adsorption process (Lomauro et al., 1985, Hossain et al., 2001, Kapsen et al., 2006, Kouhila et al., 2006, Vega-Galvez et al., 2008, Ethmane Kane et al., 2008, Idlimam et al., 2008, Li, 2012, Machhour et al., 2012).

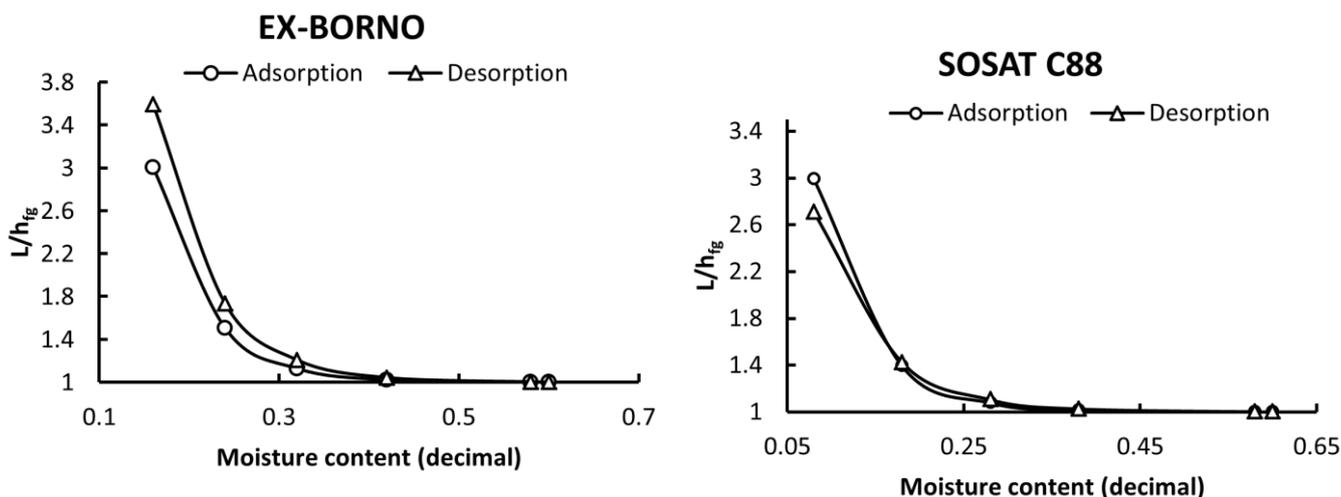


Figure 2 Effect of moisture content on L/h_{fg} for EX-BORNO and SOSAT C88 millet grains

3.3 Monolayer moisture content

The variations of BET and GAB monolayer moisture contents (M_m) of EX-BORNO and SOSAT C88 millet grains with temperature are presented in Figures 3. The monolayer moisture contents of the grains decreased with increase in temperature. This may probably be due to reduction in the number of sites available for water binding as a result of physical and chemical changes induced by temperature (Mazza and LeMaguer 1978). Similar findings were reported for soybean (Aviara et al., 2004) and corn stover fractions (Igathinathane et al., 2007).

The relationships existing between the monolayer moisture content of EX-BORNO and SOSAT C88 and temperature can be expressed by the following equations:

EX-BORNO:

BET Adsorption: $M_{mBA} = -0.206T + 23.092$ (43)

BET Desorption: $M_{mBD} = -0.1625T + 22.379$ (44)

GAB Adsorption: $M_{mGA} = -0.2591T + 25.831$ (45)

GAB Desorption: $M_{mGD} = -0.244T + 27.516$ (46)

SOSAT C88:

BET Adsorption: $M_{mBA} = -0.142T + 16.636$ (47)

BET Desorption: $M_{mBD} = -0.0999T + 15.801$ (48)

GAB Adsorption: $M_{mGA} = -0.1658T + 18.22$ (49)

GAB Desorption: $M_{mGD} = -0.1283T + 18.229$ (50)

The values for the coefficient of determination of the above Equations range from 0.97 to 0.99, where: M_m is the monolayer moisture content % (d.b.) and T is temperature °C.

It has been reported by Timmermann et al. (2001), that the GAB monolayer value is always higher than the BET value and the GAB energy constant always lower than the BET constant. However, for EX-BORNO and SOSAT C88 millet grains, at temperatures below 50 °C, the GAB monolayer moisture contents were higher than the BET values, and thereafter, the values became close. This may be an indication that as temperature increased

beyond 50 °C, the indicator of difference in free enthalpy between sorbate multilayers and pure liquid in the GAB model tended towards unity (Timmermann, 2003). The desorption values of monolayer moisture content were higher than those of adsorption for both grains. This may be attributable to the existence of moisture sorption hysteresis. The BET monolayer moisture contents (M_m) were used for further analysis.

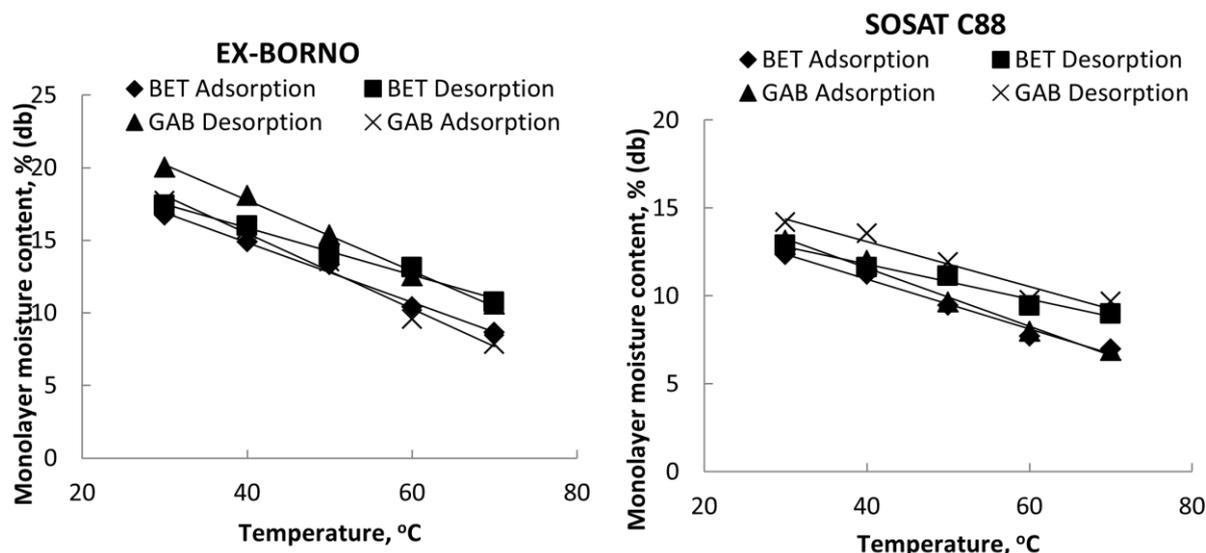


Figure 3 Variation of adsorption and desorption monolayer moisture content of EX-BORNO and SOSAT C88 millet grains calculated using the BET and GAB MSI models, with temperature

3.4 Spreading pressure

The spreading pressure isotherms of EX-BORNO and SOSAT C88 millet grains are shown in Figure 4. From the figure, it can be seen that at any temperature, the spreading pressure increased with increase in water activity and the effect of temperature did not appear to be significant. Similar observation was made by Tolaba et al. (1995), Fasina et al. (1999), Aviara et al. (2000), Aviara and Ajibola (2002), Aviara et al. 2002, Aviara et al. (2004), Arslan and Toğrul (2005) and Fasina (2006) on cereal grains and starchy materials, winged bean seed and gari, ripe and unripe plantain, melon seed and cassava, sesame seed, soya bean, macaroni and sweet potato, respectively. The adsorption spreading pressure isotherms were higher than the corresponding desorption isotherms. This may be due to the existence of hysteresis in the moisture sorption isotherms of the grains and could be an indication that the

molecules on the surface of the materials (EX-BORNO & SOSAT C88) during adsorption had more energy (Fasina et al., 1999, McMinn and Magee, 2003 and Polatoglu et al., 2010) compared to the molecules on the surface during desorption. Toğrul and Arslan (2007) however presented data that indicated that the spreading pressure of walnut kernels in desorption was higher than that of adsorption at the same temperature and water activity. The surface energies of water during adsorption and desorption were higher than that of pure water (0.072 J/m^2) at water activities above 0.20 in the two millet varieties. This implies that the grains had high surface excess energy and that this is higher than that of pure water during both adsorption and desorption processes. The SOSAT C88 grain had higher surface excess energy than the EX-BORNO. The effect of hysteresis on spreading pressure isotherms did not follow the trend that it had on

moisture sorption isotherms. In the moisture sorption isotherms, hysteresis disappeared at higher water activities, but in the spreading pressure isotherms, it increased with

increase in water activity and tended to be more profound at higher water activities.

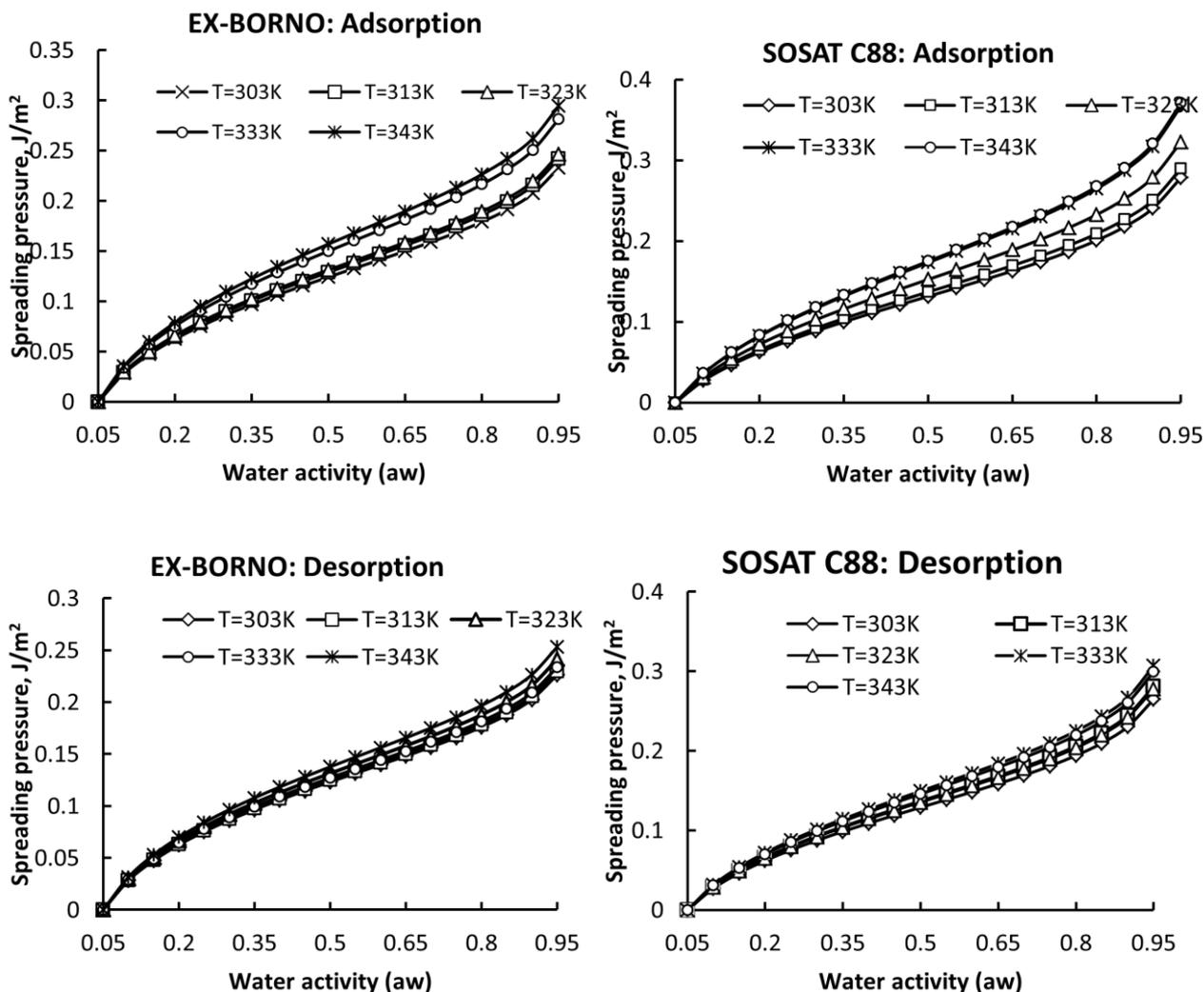


Figure 4 Spreading pressure isotherms of EX-BORNO and SOSAT C88 millet grains at different temperatures in adsorption and desorption processes

3.5 Net integral enthalpy and entropy

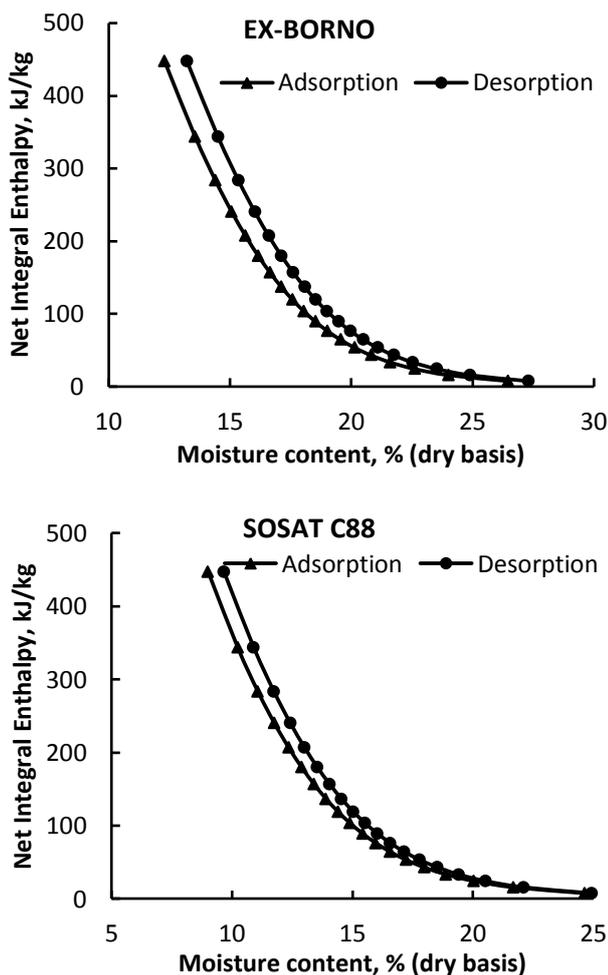
Figure 5 shows the plots of net integral enthalpy as a function of moisture content for both EX-BORNO and SOSAT C88 millet grains. The net integral enthalpy of the grains decreased with increase in moisture content. Similar findings were reported on soybean (Aviara et al., 2004), grain sorghum (Rizvi and Benado, 1983), horseradish root (Mazza, 1980), yellow globe onion (Mazza and Le Maguer, 1978), plantain (Aviara and Ajibola, 2000) and melon seed (Aviara and Ajibola, 2002).

Initial increase in enthalpy with moisture content in the lower moisture range was observed in some products like corn stover fractions (Igathinathane et al., 2007), winged bean seed and gari (Fasina et al., 1999). This was attributed to the binding of water to the most accessible sites on the solid exterior surface. Increase in moisture may have caused the material swelling and opening up of new high-energy sites for water to get bound to and this must have in turn increased the net integral enthalpy. The increase at low moisture contents continued until all binding sites were covered then, the net integral enthalpy

after reaching a maximum value declined with further increase in moisture levels as less favorable sites were covered and multiple layers of sorbed water were formed. In the case of millet, the response of integral enthalpy to moisture content may be due to the fact that as the moisture of the grains increased, the sorptive sites get saturated and water molecules become held to the particles more by surface tension than by chemical adsorption. The surface tensional forces being weaker are then easily broken, and this results in the lowering of integral enthalpy (Aviara et al., 2004). The adsorption and desorption integral enthalpy were the same at any given water activity, and followed a similar trend with moisture content, with the adsorption values lagging behind the desorption values (Arslan and Toğrul, 2005) until the trend of both of them became asymptotic (Aviara and Ajibola, 2000, 2002) after the moisture contents of 25% and 20% (db) were respectively exceeded for EX-BORNO and SOSAT C88 millet grains.

Figure 5 Variation of net integral enthalpy of EX-BORNO and SOSAT C88 millet varieties with moisture content

The variation of net integral entropy with moisture content is shown in Figure 6 for both EX-BORNO and SOSAT C88 millet grains. Net integral entropy had positive values in the moisture range below 13% for adsorption and 14% for desorption in EX-BORNO, and below 10% and 11% for adsorption and desorption respectively in SOSAT C88, and decreased with increase in moisture content till the moisture level of about 13.65% for adsorption and 14.51% for desorption, was reached in EX-BORNO, and 10.23% for adsorption and 10.9% for desorption, in SOSAT C88. From that point, the trend was reversed for the two millet varieties and it began to increase with increase in moisture content (Ajibola et al., 2005). The trend of net integral entropy with moisture content for EX-BORNO and SOSAT C88 millet grains was sinusoidal with desorption values leading the adsorption values and occurring at higher moisture content level. The decrease of entropy in the low moisture range has been attributed to lateral interactions in the adsorbed film caused by restrictive effect (loss of rotational freedom) of adsorbed water molecules as the available sites become saturated, and structural alteration of the adsorbing food towards increased crystallinity (Kapsalis, 1987). The increase in entropy after a point indicates that the newly bound water molecules are held less strongly, therefore, they possess more degrees of freedom as a result of a gradual opening and swelling of the polymer (Bettelheim, et al., 1970).



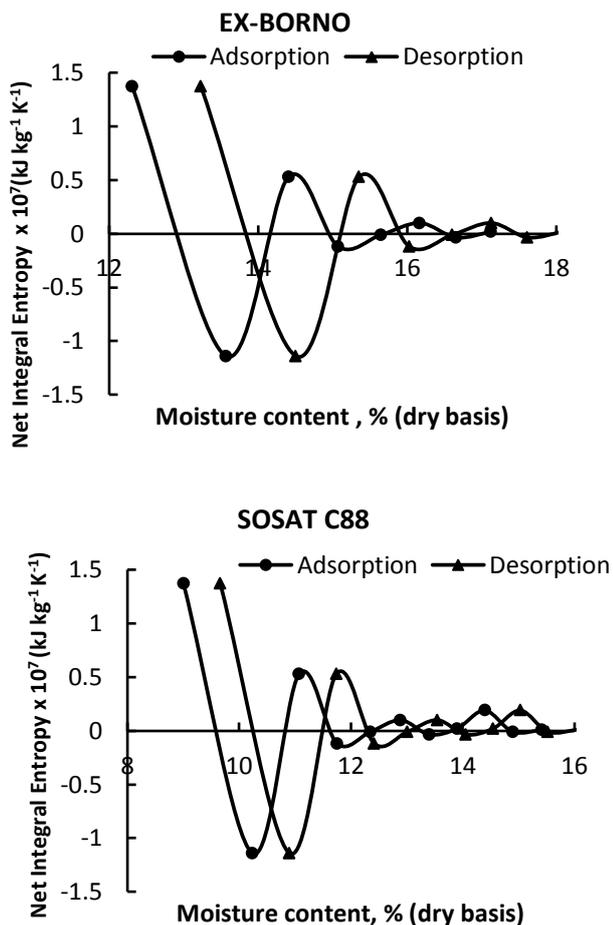


Figure 6 Variation of net integral entropy of SOSAT C88 and EX-BORNO millet varieties with moisture content

The difference between the adsorption and desorption net integral entropy trend with moisture content for the grains decreased with increase in moisture content and vanished as the moisture content of 18% (EX-BORNO) and 16% (SOSAT C88) respectively was approached. This may be due to the fact that at higher moisture contents the existence of moisture sorption hysteresis disappeared. Similar findings were reported on palm kernel (Ajibola et al., 2005) and cowpea (Ajibola et al., 2003).

3.6 Net isosteric heat of sorption (q_{st}) and differential entropy (S_a)

The variations of net isosteric heat of sorption with moisture content for EX-BORNO and SOSAT C88 millet grains in both adsorption and desorption are shown in Figure 7. As can be seen from this Figure, at low moisture levels, the net isosteric heat of sorption was higher than at

higher moisture contents. The decrease in net isosteric heat with the amount of water sorbed can be quantitatively explained by considering that at low moisture levels, sorption occurs on the most active available sites given rise to high interaction energy. As the moisture increases, water occupies the less active sites, giving lower heats of sorption. The decrease in net isosteric heat of sorption with increase in moisture content for both millet varieties was initially rapid, but after a while, remained approximately constant. Different investigators have determined the net isosteric heat in both adsorption and desorption for such products as potatoes (McLaughlin and Magee 1998); grapes (Kaymak-Ertekin and Gedik, 2004), apricots and apples (Jamali et al., 2006), corn stover fractions (Igathinathane et al., 2007), cotton seed protein isolate (Tunc and Duman, 2007) and pineapple (Simal et al., 2007). In most cases, the desorption heats were significantly higher than the adsorption values at low moisture contents, indicating that the energy required in the desorption process is higher than that in the adsorption process (Kaymak-Ertekin and Gedik, 2004). As moisture content increased the difference tended to disappear. Iglesias and Chirife (1976c) highlighted this in their review of isosteric heats.

Figure 7 also shows that at high and low moisture content levels, the values of net isosteric heat of sorption of EX-BORNO were higher than those of SOSAT C88. This indicates that lesser energy will be required to extract moisture from SOSAT C88 than from EX-BORNO. The effect of hysteresis on net isosteric heat was more pronounced in EX-BORNO than in SOSAT C88 millet grains. Several researchers have attempted to determine which branch of an isotherm that exhibits hysteresis represents the true equilibrium condition. Mazza and Le Maguer (1978) used the desorption branch as the true equilibrium in their calculations of the entropy of water in various foods.

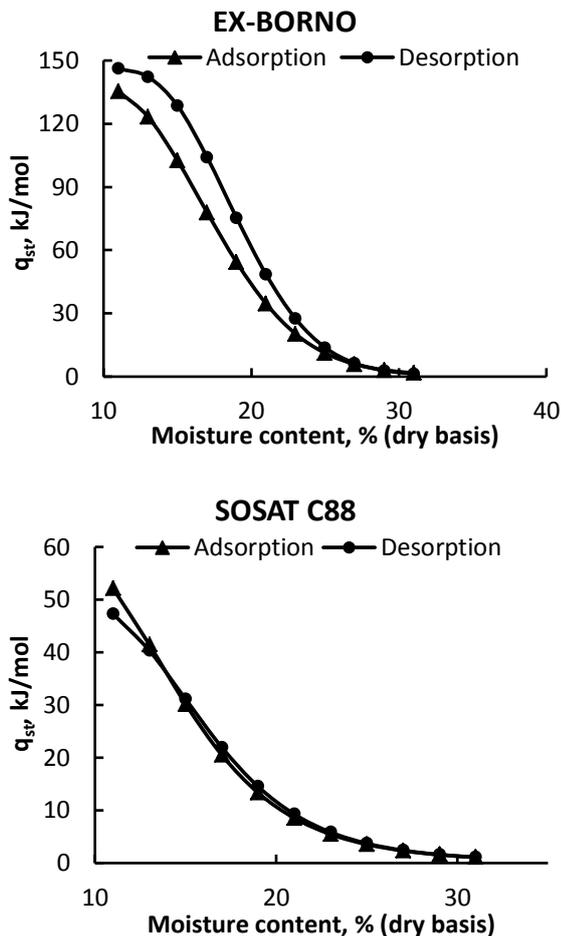


Figure 7 Variation of net isosteric heat of moisture sorption in EX-BORNO and SOSAT C88 millet grains with moisture content

The variation of differential entropy with moisture content shown in Figure 8, followed a similar trend as that of the net isosteric heat of sorption. The high interactive energy of sorption at low moisture levels may have increased the degree of randomization or disorderliness of the molecules of sorbed species and given rise to enhanced entropy. As the moisture content increased, water molecules occupy less active sites and tend toward saturation. This could in turn lower the heat of sorption and cause the entropy to decrease towards that of liquid water. There was an initial exponential decrease with increase in moisture content and a stabilization as increase in moisture content continued. Net differential entropy of moisture in desorption was higher than that of adsorption with the effect of hysteresis being more pronounced in EX-BORNO and at lower moisture content levels. As

moisture content continued to increase, the effect of hysteresis on differential entropy tended to disappear. Similar results were reported on corn stover fractions (Igathinathane et al., 2007), cotton seed protein isolate (Tunc and Duman, 2007), pineapple (Simal et al., 2007). From Figure 8, it can be seen that the values of differential entropy in EX-BORNO were higher than those of SOSAT C88. This can be attributed to the fact that SOSAT C88 is an improved variety, which attained equilibrium in both adsorption and desorption at lower moisture values.

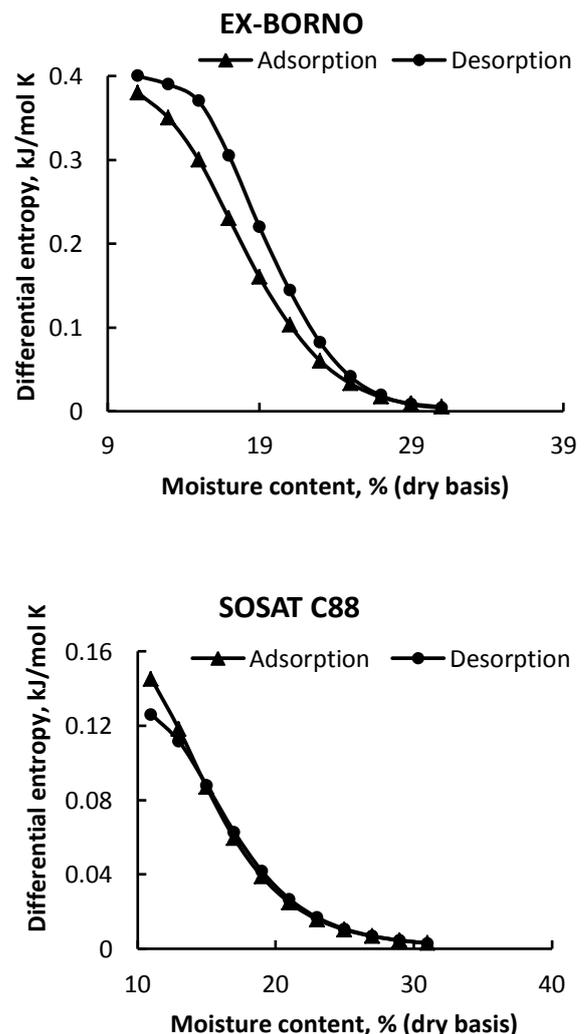


Figure 8 Variation of differential entropy in EX-BORNO and SOSAT C88 millet varieties with moisture content

3.7 Enthalpy-entropy compensation theory

The plots of isosteric heat of sorption against differential entropy (Figure 9) were linear for the two millet varieties. The linear relationships existing between

the isosteric heat and differential entropy of the millet varieties can be expressed by the following Equations:

EX-BORNO:

$$S_{da} = 343.34q_{da} + 43.344 \tag{51}$$

$$S_{dd} = 359.02q_{dd} + 42.64 \tag{52}$$

SOSAT C88:

$$S_{da} = 355.49q_{da} + 43.77 \tag{53}$$

$$S_{dd} = 367.7q_{dd} + 43.614 \tag{54}$$

The values for the coefficient of determination of the above Equations are 0.997, 0.998, 1.000 and 0.999 respectively, where: S_{da} is the differential entropy in adsorption (kJ/kMol), S_{dd} is differential entropy in desorption (kJ/kMol), q_{da} is differential enthalpy in adsorption (kJ/kMol) and q_{dd} is differential enthalpy in desorption (kJ/kMol).

Values of the constant (α) of the linear differential enthalpy-entropy fit was 43.34 kJ/mol for EX-BORNO and 43.77 kJ/mol for SOSAT C88 in adsorption, and 42.64 and 43.61 kJ/mol respectively in desorption. The Isokinetic temperatures (T_β) of EX-BORNO and SOSAT C88 were 343.34 and 355.49K for adsorption and 359 and 367.7 K for desorption respectively, and the harmonic mean temperature (T_{hm}) was 322.3 K. Inequality of these temperature values ($T_\beta \neq T_{hm}$) confirmed the enthalpy-entropy compensation theory (McMinn and Magee, 2003). As stated earlier, if the condition $T_\beta > T_{hm}$ exists, the process is said to be enthalpy driven, but if $T_\beta < T_{hm}$ is the case, the process is considered to be entropy controlled (McMinn et al., 2005). From the results given above, it can be seen that the T_β values are higher than T_{hm} , therefore, moisture sorption processes in EX-BORNO and SOSAT C88 millet grains were considered to be enthalpy driven. Other investigators reported values of T_β and T_{hm} as 348 and 317.2 K for garlic (Madamba et al., 1996), 376.6 K in adsorption, 372.8 K in desorption and 317.5 K for potato (McMinn and Magee, 2003, McMinn et al., 2005), 461.1-570.4 K and 302.7 K for cotton seeds and kernels Tunc and Duman, 2007), 324.31-372.68 K and 299.5 K for corn stover fractions (Igathinathane et al.,

2007), 342 and 297.5 K for pineapple (Simal et al., 2007), 323.4 and 292.8K for sucuk (Polatoglu et al., 2010), 340.99-373.77 K and 301.585 K for almond varieties (Taitano and Singh, 2012), 294.6 K fresh and 297 ripened and 281.1 K for Mexican Mennonite-style cheese (Martinez-Monteaquedo and Salais-Fierro, 2014) and 361.32 and 329.18 K for prickly pear seeds (Hassini et al., 2015). Each of the above investigations showed moisture sorption in the products to be enthalpy driven. Bernstein and Norena (2015) however, noted that moisture sorption in red cabbage aqueous extract encapsulated in gum Arabic and spray dried was entropy driven.

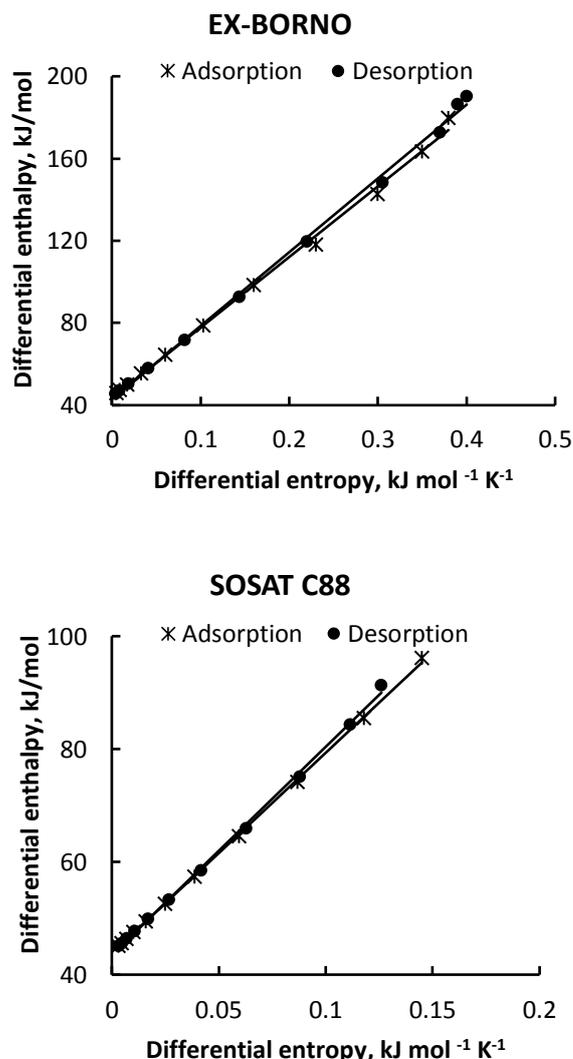


Figure 9 Plots of isosteric heat of sorption (differential enthalpy) against differential entropy for EX-BORNO and SOSAT C88 millet varieties

4 Conclusions

The investigation of sorption thermodynamic characteristics of EX-BORNO and SOSAT C88 millet grains in adsorption and desorption at five different temperatures (30 °C, 40 °C, 50 °C, 60 °C and 70 °C) revealed the following:

(1) The modified Oswin moisture sorption isotherm model with the highest coefficient of determination and least standard error, proved the best for predicting the water activity of the two millet varieties.

(2) Latent heat of moisture sorption decreased with increase in moisture content in both adsorption and desorption, and attained the free water point between the moisture contents of about 38% in adsorption and 42% in desorption for EX-BORNO, and 32% in adsorption and 34% in desorption for SOSAT C88. The effect of hysteresis on the ratio of heat of moisture sorption to the latent heat of pure water decreased with increase in moisture content and completely disappeared at higher moisture levels.

(3) Monolayer moisture contents of the two millet varieties in both adsorption and desorption decreased with increase in temperature, with the desorption values higher than the adsorption values as a result of hysteresis. Monolayer moisture contents calculated using the GAB model, were not significantly higher than those obtained using the BET model.

(4) The surface potential (spreading pressure) of moisture in the grains increased with increase in water activity and the effect of temperature was not significant. The effect of hysteresis was more apparent at higher temperatures and water activities.

(5) Net integral enthalpy decreased with increase in moisture content with the effect of hysteresis on it also decreasing with increase in moisture content. Net integral entropy decreased with increase in moisture to a certain value of moisture level and thereafter, no further increase occurred. The trend of net integral entropy with moisture content for the two millet varieties was sinusoidal with the

desorption trend occurring at higher moisture content level.

(6) Net isosteric heat of sorption and differential entropy of the two millet varieties decreased with increase in moisture content.

(7) Isokinetic temperatures (>340 K) were greater than harmonic mean temperature (322.3 K) of the two millet varieties, and this inequality confirmed the enthalpy-entropy compensation theory. The moisture sorption processes were predominantly enthalpy driven.

(8) Moisture sorption hysteresis affected all the thermodynamic properties determined and the effects were more pronounced at higher temperatures, higher water activities and lower moisture content levels.

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