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Thermodynamic properties of water desorption of forage turnip seeds

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ABSTRACT. The purpose of this study was to determine the thermodynamic properties of the process of water sorption in forage turnip seeds. The equilibrium moisture content of forage turnip seeds was determined by the gravimetric-dynamic method for different values of temperature and water activity. According to the results, increasing the moisture content increases the energy required for the evaporation of water in forage turnip seeds, and the values of integral isosteric heat of desorption, within the moisture content range of 3.33 to 11.30 (% d.b.), varies from 4,222.70 to 2,870.34 kJ kg^{-1}. With the elevation in the equilibrium moisture content, there is an increase in differential entropy and Gibbs free energy, which has positive values, demonstrating non-spontaneity in the process of desorption in the seeds. The theory of enthalpy-entropy compensation can be satisfactorily applied to the sorption phenomenon, and the process of water desorption of forage turnip seeds is controlled by enthalpy.

Keywords: hygroscopic equilibrium, isosteric heat, gibbs free energy, compensation theory.

Propriedades termodinâmicas de dessorção de água das sementes de nabo forrageiro

RESUMO. O objetivo do presente trabalho foi determinar as propriedades termodinâmicas do processo de sorção de água em sementes de nabo forrageiro. O teor de água de equilíbrio das sementes de nabo forrageiro foi determinado pelo método dinâmico-gravimétrico para diferentes valores de temperatura e atividade de água. De acordo com os resultados encontrados, observou-se que com o incremento do teor de água ocorre aumento da energia necessária para a evaporação da água nas sementes de nabo forrageiro, sendo que os valores do calor isostérico integral de dessorção, na faixa de teor de água de 3,33 a 11,30 (% b.s.), variam de 4.222,70 a 2.870,34 kJ kg^{-1}. Com a elevação do teor de água de equilíbrio há um aumento da entropia diferencial e da energia livre de Gibbs que apresenta valores positivos demonstrando não-espontaneidade no processo de dessorção nas sementes. A teoria de compensação entalpia-entropia pode ser satisfatoriamente aplicada ao fenômeno de sorção, sendo o processo de dessorção da água das sementes de nabo forrageiro controlados pela entalpia.

Palavras-chave: equilíbrio higroscópico, calor isostérico, energia livre de Gibbs, teoria da compensação.

Introduction

Forage turnip (*Raphanus sativus* L.) is a plant originally from East Asia and Europe, belonging to the Brassicaceae family. The cultivation of forage turnip has become advantageous because its seeds have significant levels of non-edible oils that are easily extracted. In addition, the forage turnip has productive potential in times of little utilisation or fallowing arable lands and can also be used as vegetal cover in the intervals between crops of other species.

The quality of the grains is an important parameter for marketing and processing and can significantly affect the value of the product. Despite all current available technology, the qualitative and quantitative losses arising during the post-harvest process are not yet fully controlled, and during storage, the grain mass is constantly subjected to external factors. These factors can be physical, such as temperature and air relative humidity, chemical, such as the oxygen supply, and biological, such as bacteria, fungi, insects and rodents (BROOKER et al., 1992).

The moisture content of the agricultural products is extremely important to show the interactions between water molecules and the compounds of the product (GHODAKE et al., 2007), and it is directly related to the drying and storage processes of these agricultural products.

With high levels of water, the risk of fungal and insect infestation becomes greater, seriously impairing the germination power and vigour of the seeds, deteriorating the quality of the stored fruits and seeds and increasing post-harvest losses. However, a reduction in moisture content promotes economic losses due to mass loss of the product (YAZDANI et al., 2006) while reducing the biological activity of the product and chemical and physical changes that occur during storage.

The thermodynamic properties of water desorption are crucial for evaluating the design of the equipment involved in several processes of preservation, drying, storage, packaging and mixing of food (AVIARA et al., 2004; ASCHERI et al., 2009; KAYA; KAHYAOGLU, 2006). They are easily calculated because they relate the equilibrium moisture content of the product with the surrounding medium at a certain temperature and water activity. They are determined through sorption isotherms and allow the experimental results to be read in accordance with the theory (CHEMKHIA et al., 2004; KAYA; KAHYAOGLU, 2006).

According to Wang and Brennan (1991), to remove the water associated with hygroscopic material, the energy required is greater than that used to vaporise the same amount of free water under the same conditions of pressure and temperature. The additional energy, due to the binding forces between the water and the surface of the adsorbent substance, is known as the isosteric heat of desorption in drying processes and is a good parameter for estimating the minimum amount of heat required to remove a given amount of water from the product.

Differential enthalpy is used to design driers capable of providing heat above the latent heat of vaporisation of pure water to dry the material at low levels of moisture content (TSAMI et al., 1990). Differential entropy is related to the number of sorption sites for a given energy level inherent in the biological material (MADAMBA et al., 1996) and is used to obtain information regarding energy rationalisation during the processing, dissolution and crystallisation of the product (AVIARA et al., 2002).

Integral quantities allow the qualitative interpretation of the sorption phenomenon. They describe the degree of disorder and disordered motion for the water molecules as well as the energy involved in the sorption processes. These functions derive from the first law of thermodynamics applied to pure adsorbent material (RIZVI, 1986).

The viability and range of a chemical reaction is best determined by measuring the changes in Gibbs free energy, i.e., water vaporisation during the dehydration process (TELIS et al., 2000).

Recently, studies are being conducted to determine the thermodynamic parameters, such as enthalpy, entropy, Gibbs free energy and isosteric heat, for different oilseeds products, such as sesame seed (*Sesamum indicum* L.) (KAYA; KAHYAOGLU, 2006), peanut (*Arachis hypogaea* L.) (CORRÊA et al., 2007), macadamia (*Macadamia integrifolia* Maid. and Bet.) (DOMINGUEZ et al., 2007) and cocoa beans (*Theobroma cacao* L.) (OLIVEIRA et al., 2011).

Therefore, this study aimed to determine the thermodynamic properties of forage turnip seeds for the process of water desorption.

Material and methods

This study was conducted in the Laboratory of Postharvest of Vegetable Products from the Federal Institute of Education, Science and Technology of State Goias (Instituto Federal de Educação, Ciência e Tecnologia Goiano – IF Goiano) - Rio Verde Câmpus, located in the municipality of Rio Verde, Goias State.

We used manually collected forage turnip seeds with a moisture content of approximately 36% d.b.

To obtain the moisture content of seeds at hygroscopic equilibrium, the dynamic-gravimetric method was used. The desorption of the product in a thin layer was conducted under different controlled conditions of temperature (25, 30, 35, and 40°C) and relative humidity (from 20 to 80%) until the product reached its equilibrium moisture content under the specified air condition.

The environmental conditions for the testing of hygroscopicity tests were provided through an atmospheric conditioning chamber. The samples, each containing 10 g of product, were surrounded by a permeable fabric (cheesecloth type) to allow air flow through the seeds and were placed in the apparatus. The temperature and relative humidity of the air were monitored by a psychrometer installed close to the trays containing the samples.

During the process, the samples were periodically weighed. The hygroscopic equilibrium was reached when the mass changes remained approximately invariable over three consecutive weighings at intervals of 24 hours.

The moisture content was determined gravimetrically, with the oven at 105±1°C for 24 hours, in two repetitions (BRASIL, 2009).

The value of the water activity of forage turnip was obtained using the Copace equation shown below:

$$Xe = \exp\left\{1.335028^{**} - \left(0.016934^{**} \times T\right) + \left(1.979293^{**} \times a_w\right)\right\} \quad (1)$$

**Significant at 1% by t test.

where:

Xe: equilibrium moisture content,% d.b.;

a_w: water activity, decimal;

T: temperature, °C.

The net isosteric heat of desorption (or differential enthalpy) for each equilibrium moisture content was calculated using the Clausius-Clayperon equation (IGLESIAS; CHIRIFE, 1976):

$$\frac{\partial \mathrm{In}\left(a_w\right)}{\partial T}=\frac{\Delta h_{st}}{RT_a^2} \qquad (2)$$

where:

T_a: absolute temperature, K;

Δh_{st}: differential enthalpy, kJ kg^{-1};

R: universal gas constant for water vapour 0.4619 kJ kg^{-1} K^{-1}.

Integrating Equation 2 and assuming that the liquid isosteric heat of sorption is independent of the temperature, the net isosteric heat of desorption for each equilibrium moisture content was obtained according to the following equation (WANG; BRENNAN, 1991):

$$\mathrm{In}\left(a_w\right)=-\left(\frac{\Delta h_{st}}{R}\right)\times\frac{1}{T_a}+C \qquad 3)$$

where:

C: model coefficient.

The integral isosteric heat of desorption was obtained by adding the value of the latent heat of vaporisation of free water according to Equation 5 to the value of the net isosteric heat of sorption:

$$Q_{st}=\Delta h_{st}+L=a\times\exp\left(-b\times Xe\right)+c \qquad (4)$$

where:

Q_{st}: integral isosteric heat of sorption, kJ kg^{-1};

a, b and c: coefficients of the model.

The latent heat of vaporisation of free water (L), in kJ kg^{-1}, required to calculate Q_{st} was obtained with the average temperature (T) in the studied range, in °C, using the following equation:

$$L = 2502.2 - 2.39\times T \qquad (5)$$

where:

L: latent heat of vaporisation of free water, kJ kg^{-1}.

The differential entropy of sorption was calculated using the Gibbs-Helmholtz equation shown below (RIZVI, 1995):

$$\Delta S=\frac{\Delta h_{st}\Delta G}{T_a} \qquad (6)$$

where:

ΔS: differential entropy of sorption (kJ $kg^{-1}K^{-1}$);

ΔG: Gibbs free energy (kJ kg^{-1}).

The Gibbs free energy can be calculated through the following equation:

$$\Delta G=-R\times T\times \mathrm{In}(aw) \qquad (7)$$

The effect of the changes in the sorption of water on free energy is usually followed by changes in the values of enthalpy and entropy. Thus, when we substitute Equation 7 in Equation 6 and rearrange the resulting equation, we have the following:

$$\mathrm{In}(aw)=\frac{\Delta h_{st}}{R\times T_a}-\frac{\Delta S}{R} \qquad (8)$$

The values of the differential enthalpy and entropy of sorption were calculated using Equation 8. The calculated values of enthalpy (Δ_{hst}) and entropy (ΔS) were correlated with the following equation (BERISTAIN et al., 1996):

$$\Delta h_{st}=T_B(\Delta S)+\Delta G_B \qquad (9)$$

where:

T_B: isokinetic temperature (K);

ΔG_B: Gibbs free energy at isokinetic temperature (kJ kg^{-1}).

The isokinetic temperature is the temperature at which the reactions in a series occur at the same rate. Given that enthalpy and entropy are correlated, the compensation theory is assumed to be valid for the sorption (BERISTAIN et al., 1996). To confirm the existence of this compensation, the isokinetic temperature was compared with the harmonic mean of the temperatures used to determine the sorption isotherms, according to Equation 10 (KRUG et al., 1976a and b):

$$T_{hm}=\frac{n}{\sum\left(\frac{1}{T}\right)} \qquad (10)$$

where:

T_{hm}: harmonic mean of temperature (K);

n: number of temperatures used.

According to Krug et al. (1976a and b), the linear chemical compensation or compesantion theory exists only if the isokinetic temperature (T_B) is different from the harmonic mean of the temperature (T_{hm}). An approximate confidence interval, (1-α) 100%, for the isokinetic temperature was calculated with the following equation:

$$T_B = \hat{T} \pm t_{m_p-2,\alpha/2} \sqrt{Var(\hat{T}_B)} \quad (11)$$

where:

$$\hat{T}_B = \frac{\sum\left(\Delta h_{st} - \overline{\Delta h_{st}}\right)\left(\Delta S - \overline{\Delta S}\right)}{\sum\left(\Delta S - \overline{\Delta S}\right)^2} \quad (12)$$

and,

$$Var(T_B) = \frac{\sum\left(\Delta h_{st} - \overline{\Delta G_B} - \hat{T}_B \Delta S\right)^2}{(m_p - 2)\sum\left(\Delta S - \overline{\Delta S}\right)^2} \quad (13)$$

where:

m_p: number of pairs of data on enthalpy and entropy;

$\overline{\Delta h_{st}}$: mean enthalpy, kJ kg^{-1};

$\overline{\Delta S}$: mean entropy kJ kg^{-1}.

If the harmonic mean of the temperature is in the estimated interval of the isokinetic temperature T_B, the relationship between the values of sorption differential enthalpy and entropy reflect only experimental errors and not the existence of chemical and physical factors that guide the compensation theory (BERISTAIN et al., 1996). For T_B, we adopted a confidence interval of 95% for the range of data studied.

Results and discussion

The mean values of the moisture content of hygroscopic equilibrium of the forage turnip seeds obtained by desorption at temperatures of 25, 30, 35, and 40°C and water activity from 0.27 to 0.82 (decimal) are shown in Table 1:

Table 1. Mean values of equilibrium moisture content (% d.b.) of forage turnip, obtained by desorption process, as a function of temperature (°C) and water activity (decimal, ± 0.03).

Temperature (°C)	Water activity (decimal)									
	0.27	0.30	0.37	0.40	0.45	0.52	0.67	0.75	0.77	0.82
25	-	5.04	-	-	6.60	6.95	-	10.88	-	-
30	-	-	4.57	-		6.36	8.42	-	10.21	-
35	-	-	4.36	-	-	5.83	7.92	-	-	11.30
40	3.33	-	-	3.61	-	5.69	7.54	-	-	-

Table 1 shows that for the same temperature, with variation in the water activity, there is a significant increase in the equilibrium moisture content for forage turnip seeds.

Figure 1 presents the curves of the neperian logarithm of water activity (decimal) calculated using the Copace equation for the specific values of equilibrium moisture content (% d.b.) as a function of the values of the inverse of the absolute temperature (K) for forage turnip seeds.

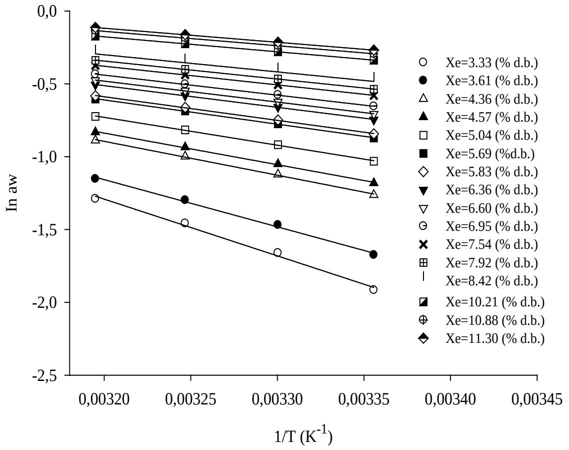

Figure 1. Curves of the neperian logarithm of the water activity (decimal) for specific values of equilibrium moisture content (% d.b.) as a function of the values of 1 T^{-1} (K^{-1}) for forage turnip seeds.

The values of differential enthalpy (Δh_{st}), in kJ kg^{-1}, for forage turnip seeds as a function of the equilibrium moisture content (% d.b.) were calculated according to Equation 3 and are represented for each condition by the slopes of the lines in Figure 1. These values are shown in Table 2.

Table 2. Linear equations of the neperian logarithm of water activity (decimal) as a function of the inverse absolute temperature (1 T^{-1} K^{-1}) for different values of the equilibrium moisture content (% d.b.) of forage turnip seeds.

Xe (% d.b.)	Linear equation	Xe (% d.b.)	Linear equation
3.33	$\ln(a_w) = 11.166 - 3893.1 \times \frac{1}{T}$	6.60	$\ln(a_w) = 4.1212 - 1438.3 \times \frac{1}{T}$
3.61	$\ln(a_w) = 9.2127 - 3240.7 \times \frac{1}{T}$	6.95	$\ln(a_w) = 3.9549 - 1373.4 \times \frac{1}{T}$
4.36	$\ln(a_w) = 6.5434 - 2324.4 \times \frac{1}{T}$	7.54	$\ln(a_w) = 3.7271 - 1283.1 \times \frac{1}{T}$
4.57	$\ln(a_w) = 6.109 - 2170.9 \times \frac{1}{T}$	7.92	$\ln(a_w) = 3.6047 - 1233.8 \times \frac{1}{T}$
5.04	$\ln(a_w) = 5.3855 - 1911.1 \times \frac{1}{T}$	8.42	$\ln(a_w) = 3.4648 - 1176.5 \times \frac{1}{T}$
5.69	$\ln(a_w) = 4.7159 - 1664.5 \times \frac{1}{T}$	10.21	$\ln(a_w) = 3.1147 - 1028.6 \times \frac{1}{T}$
5.83	$\ln(a_w) = 4.6056 - 1623.1 \times \frac{1}{T}$	10.88	$\ln(a_w) = 3.0212 - 987.68 \times \frac{1}{T}$
6.36	$\ln(a_w) = 4.2528 - 1489.1 \times \frac{1}{T}$	11.30	$\ln(a_w) = 2.9706 - 965.19 \times \frac{1}{T}$

For the integral isosteric heat of desorption (Q_{st}), in kJ kg^{-1}, the value of the latent heat of vaporisation of free water (L), which represents the minimum amount of energy required for water evaporation, calculated for the average temperature of 32.5°C, was added to Δh_{st}, resulting in the value of 2,424.52 kJ kg^{-1}.

Figure 2 shows the values of integral isosteric heat of desorption (Q_{st}) as a function of the equilibrium moisture content (% d.b.), estimated according to Equation 10.

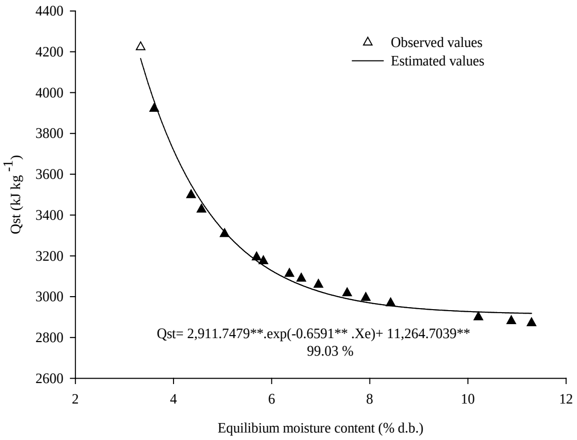

Figure 2. Estimated and experimental values of the integral isosteric heat of desorption as a function of the equilibrium moisture content. **Significant at 1% by t test.

Figure 2 shows that the reduction in the moisture content increases the energy required to remove water from the product, represented by the values of integral isosteric heat of desorption (Q_{st}), as observed for different vegetables such as quinoa (TOLABA et al., 2004), food groups (KUMAR et al., 2005), beans (RESENDE et al., 2006), sweet potato (FASINA, 2006), nutritionally enriched cactus (CAMPOS et al., 2009), the leaves and stems of dehydrated cilantro (SILVA et al., 2010), sweet corn (OLIVEIRA et al., 2010), cassava flour (AYALA-APONTE, 2011) and dehydrated passion fruit pulp (CATELAM et al., 2011). Brooker et al. (1992) claimed that the amount of energy required to remove water from seeds with low moisture content is greater than that required for moist products. According to Aviara and Ajibola (2002), these results confirm the observation that the binding force between the water molecules and dry matter is significantly reduced in products with higher water content.

The values of the integral isosteric heat of desorption for forage turnip seeds in the moisture content range from 3.33 to 11.30 (% d.b.) ranged from 4,222.70 to 2,870.34 kJ kg^{-1}.

Knowledge of the magnitude of the integral isosteric heat of sorption, for a given amount of water, provides an indication of the state of the water sorbed into the product and serves as a measure of the physical, chemical and biological stability under a given storage condition (MCMINN; MAGEE, 2003).

Thus, the elevated value of the integral isosteric heat of sorption for low values of moisture content can be explained by the differences in the binding forces of the water with the adsorbent surface of a product. In the initial stages of sorption, i.e., with a low water content, there are highly active polar sites of sorption with an elevated energy of interaction on the adsorbent surface, and these polar sites are covered with water molecules forming a monomolecular layer (AL-MUHTASEB et al., 2004). As water molecules chemically bind to active sorption sites, the sorption begins to occur at less active sites with a high moisture content, lower interaction energy and, consequently, lower isosteric heat of sorption (WANG; BRENAN, 1991).

Figure 3 shows the values of the Gibbs free energy for each temperature as a function of the moisture content of the forage turnip seeds, calculated using Equation 7.

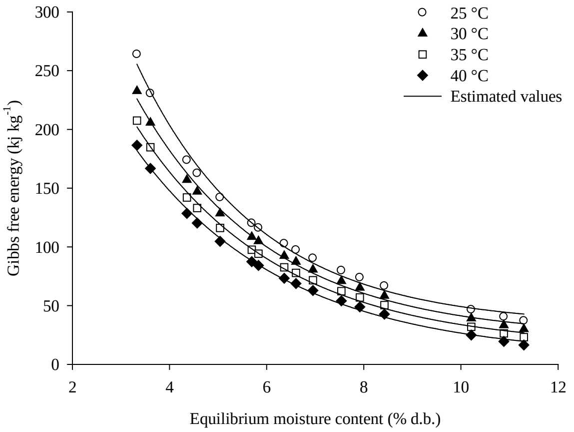

Figure 3. Gibbs free energy as a function of the equilibrium moisture content of forage turnip seeds.

From a thermodynamic standpoint, the Gibbs free energy of a product is the indicative parameter of affinity between the product and water because it provides information on the spontaneity when the Gibbs free energy is negative, entropy is positive and enthalpy is negative or on the non-spontaneity when entropy is negative and enthalpy is positive and thus the Gibbs free energy is necessarily positive (MCMINN et al., 2005; TELIS et al., 2000).

The change in the Gibbs free energy during the water exchange between a product and its medium is the energy required to transfer the water molecules from the gas state to a solid surface or vice versa. This amount may be considered as the measure of the work performed by the system to conduct the desorption or adsorption process.

Equilibrium is achieved when the gradient of Gibbs free energy is zero (NAYAK; PANDEY, 2000).

Ho and McKay (2003) explain this phenomenon by the higher energy of the adsorbate particles at higher temperatures. The 'escape' rate of the adsorbent surface would be higher, causing a reduction in the adsorption efficiency of the material.

Figure 3 shows that with increased equilibrium moisture content, there is an increase in the value of Gibbs free energy. Positive ΔG values are a characteristic of an endergonic reaction, in which the reaction requires an input of energy from the medium for water desorption from the seeds to occur. These results agree with those found by Goneli et al. (2010), who obtained smaller available sorption sites for high values of the equilibrium moisture content of okra seeds. Therefore, less work was necessary to make those sites accessible, with low values of Gibbs free energy, which was positive for all studied temperatures from 10 to 50°C.

Figure 3 shows that the phenomenon's behaviour for each temperature can be described by the following equation:

$$\Delta G = a \times \exp\left(-b \times Xe\right) + c \tag{14}$$

where:

a, b and c: coefficients of the equation.

Table 3 presents the equations fit to the values of Gibbs free energy as a function of the equilibrium moisture content (% d.b.) for each temperature tested during desorption in the forage turnip seeds.

Table 3. Exponential regressions of Gibbs free energy (kJ kg^{-1}) as a function of the equilibrium moisture content (% d.b.) of forage turnip seeds.

Temperature (°C)	Equation	R^2 (%)
25	$\Delta G = 33.3458^{**} + 829.9038^{**} \exp\left(-0.3959^{**} \times X_e\right)$	99.41
30	$\Delta G = 23.4438^{**} + 680.5346^{**} \exp\left(-0.3640^{**} \times X_e\right)$	99.54
35	$\Delta G = 14.4671^{**} + 583.0741^{**} \exp\left(-0.3405^{**} \times X_e\right)$	99.63
40	$\Delta G = 6.1274^{NS} + 514.0807^{**} \exp\left(-0.3223^{**} \times X_e\right)$	99.69

**Significant at 1% by t test, ^{NS}Not Significant.

Figure 4 shows the values of the differential entropy of desorption in kJ kg^{-1} K^{-1} as a function of the equilibrium moisture content (% d.b.).

Figure 4 shows a strong dependence of the differential entropy values on the moisture content, similar to the trend of the integral isosteric heat of sorption. There was a reduction in the values of differential entropy, with a tendency to stabilise at higher moisture contents. According to Madamba et al. (1996), these results indicate that up to a certain moisture content, the sorption processes are reversible.

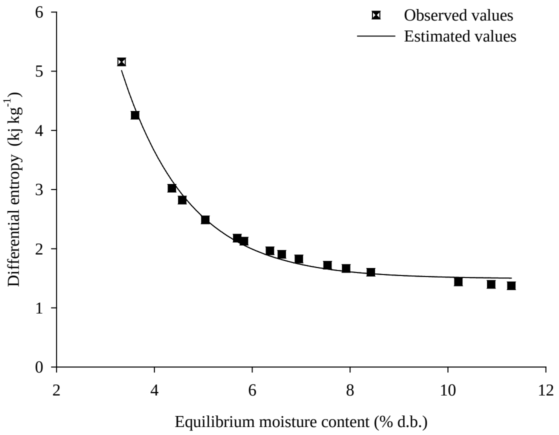

Figure 4. Estimated and experimental values of the differential entropy of the desorption of forage turnip seeds. **Significant at 1% by t test.

Figure 5 shows the values of differential enthalpy as a function of the values of the differential entropy of sorption for the desorption process of forage turnip seeds, as determined by Equation 8 for each equilibrium moisture content. We considered that for a given value of the moisture content, the differential enthalpy and entropy do not vary with temperature (AGUERRE et al., 1986).

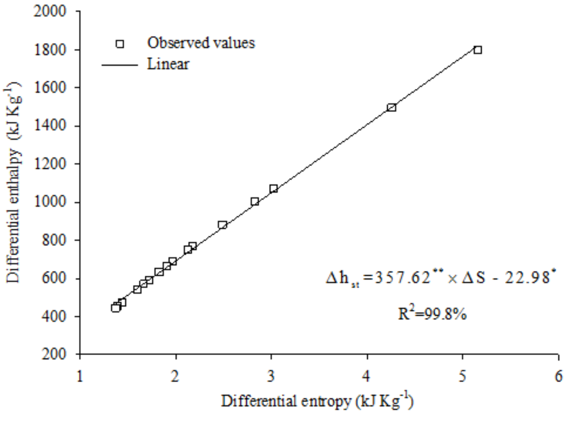

Figure 5. Enthalpy – entropy relationship for the process of water desorption from forage turnip seeds. **Significant at 1% by t test; *Significant at 5% by t test.

A linear relationship was shown for the desorption process, with a coefficient of determination (R^2) greater than 99%. As there is a high level of linearity between the values of differential enthalpy (Δh_{st}) and entropy (ΔS) of sorption, the enthalpy-entropy compensation theory, or isokinetic theory, can be considered valid for the phenomenon of the desorption of water from forage turnip seeds.

To test the validity of the enthalpy-entropy compensation theory, the isokinetic temperature was compared with the harmonic mean (T_{hm}) from the temperature range studied and used to determine the desorption process of forage turnip seeds. Enthalpy-entropy linear compensation is valid if the process is controlled by enthalpy when $T_B > T_{hm}$ or the process is controlled by entropy when $T_B < T_{hm}$ (GABAS et al., 2005).

The isokinetic temperature for the desorption of forage turnip seeds was 357.62±12.39 K. The calculated harmonic mean was 304.67 K, which is significantly different from the isokinetic temperature values described, confirming the phenomenon of the enthalpy-entropy compensation for the desorption process of forage turnip seeds. According to Liu and Guo (2001), the isokinetic temperature is that for which the reactions in series in the product should occur simultaneously, i.e., when it is in equilibrium.

Therefore, the mechanism of water desorption from forage turnip seeds can be controlled by enthalpy. These results are in agreement with various researchers who have successfully applied the isokinetic theory to the sorption of different products (CLADERA-OLIVERA et al., 2008; GONELI et al., 2010; MCMINN et al., 2005; MOREIRA et al., 2008; TELIS-ROMERO et al., 2005; TUNC; DUMAN, 2007).

Conclusion

With an increased equilibrium moisture content, there is an increase in the energy required for water evaporation in forage turnip seeds and an increase in differential entropy.The values of integral isosteric heat of desorption in the moisture content range of 3.33 to 11.30 (% d.b.) varied from 4,222.70 to 2,870.34 kJ kg^{-1}.The Gibbs free energy tended to increase with the elevation of the equilibrium moisture content, and its values were positive, demonstrating non-spontaneity in the desorption process.The enthalpy-entropy compensation theory, can be satisfactorily applied to the sorption phenomenon, and the process of water desorption seeds is controlled by enthalpy.

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