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Moisture sorption isotherms of castor beans. Part 2: Thermodynamic properties

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Key words:
Ricinus communis L.
moisture content
enthalpy–entropy compensation theory

ABSTRACT

Knowledge on the water sorption within agricultural products is extremely important for decision making during post-harvest procedures. In order to improve this knowledge, thermodynamic properties regarding water sorption provide useful data. Thermodynamic properties of castor beans, related to sorption, were determined. Static gravimetric technique under different conditions of temperature (25, 35, 45 and 55 ± 1 °C) was used. Saturated salt solutions in the range of 37-87% ± 2% were utilized to create the required controlled humidity environment. After the sorption procedure, differential enthalpy, differential entropy and Gibbs free energy of this process were calculated and decreased with increased values of equilibrium moisture content.

Palavras-chave:
Ricinus communis L.
teor de água
teoria de compensação entalpia-entropia

Isotermas de sorção de grãos de mamona. Parte 2: Propriedades termodinâmicas

RESUMO

O conhecimento da sorção de água pelos produtos agrícolas é extremamente importante para a tomada de decisões durante os procedimentos pós-colheita; visando aperfeiçoar este conhecimento as propriedades termodinâmicas relativas à sorção de água fornecem dados úteis. Propriedades termodinâmicas de grãos de mamona relacionadas à sorção, foram determinadas. A técnica de gravimetria estática em diferentes temperaturas (25, 35, 45 e 55 ± 1 °C) foi usada e soluções salinas saturadas na faixa de 37-87% ± 2% foram utilizadas para criar o requerido ambiente controlado de umidade relativa. Entalpia diferencial, entropia diferencial e energia livre de Gibbs foram calculadas e decresceram com o aumento dos valores de teor de água de equilíbrio.

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INTRODUCTION

Castor beans (*Ricinus communis* L.) come from an oleaginous plant of relevant economic and social importance. It is a crop found in several regions in Brazil, being traditionally produced at small- and average-size properties, generating employment and revenue. Besides, it has a high potential of use in biodiesel production, becoming a promising agribusiness (Florin et al., 2012).

The use of castor beans requires several post-harvest procedures, such as drying and storage. In order to perform adequately these operations, it is necessary the knowledge on the relationship between temperature and relative humidity of the air, along with the desirable conditions of the products conservation. For this purpose, equilibrium moisture content must be known under several environmental conditions. It is useful in the determination of moisture loss or gain in a certain condition of temperature and relative humidity, relating directly with drying and storage (Hessini et al., 2015).

Thermodynamic properties in sorption processes provides more information, allowing a higher understanding on the properties of water molecules and aiding the energy calculation regarding heat and mass transfer of biological systems. Also, these properties provide useful information for the development and improvement of dryers and for studies on water properties on food surface (Oliveira et al., 2011). Recently, thermodynamic parameters, such as enthalpy, entropy, Gibbs free energy and isosteric heat, among others, were investigated in different products (Moreira et al., 2008; Goneli et al., 2010a,b; Thys et al., 2010; Cladera-Olivera et al., 2011; Noshad et al., 2012; Goneli et al., 2013; Hessini et al., 2015); however, thermodynamic properties regarding water sorption of castor beans were not investigated.

In view of the importance to acknowledge and understand the moisture movement within castor beans and to provide data for the industry to improve drying equipment, this work aimed to calculate the thermodynamic properties at different moisture levels of the sorption process of castor beans.

MATERIAL AND METHODS

The present work was conducted in the Laboratory of Evaluation of Physical Properties and Quality of Agricultural Products of the National Grain Storage Training Center – CENTREINAR, Federal University of Viçosa, Viçosa, MG, Brazil.

Castor beans (cv. Guarani) were used. They were acquired at commercial farms from Divino city (MG, Brazil). Plantation was monitored during its growing cycle, every 15 days, regarding fertilizer, water demand and plant development, in order to obtain high quality products.

Two lots were used: the first one containing castor beans with initial moisture content of 82% (d.b.) for desorption process; and the second lot, which was harvested when castor beans had moisture content of approximately 7% (d.b.), in order to perform adsorption procedure. The second lot was dried in an oven with forced air circulation, at 80 °C, until a final moisture content of 2.5% (d.b.). This procedure had the goal to increase data points regarding adsorption process. In both lots, fruits were collected from the medium part of the first plant bunch.

Fruits were then homogenized and stored in low-density polypropylene bags and immediately transported to Viçosa city (MG, Brazil). Beans were manually removed from the fruits.

Different conditions of temperature (25, 35, 45 and 55 ± 1 °C) and relative humidity (between 37 and 87 ± 2%) were used for sorption processes. These conditions were provided by an atmosphere control unit (Aminco-Aire 150⁄300). Removable perforated trays were placed inside the apparatus to allow air to pass through the samples, each containing 50 g of product. Airflow was monitored with rotating blades and kept around 4 m^3 min^{-1} m^{-2}. Temperature and air relative humidity were monitored using a psychrometer installed next to the trays containing the samples.

The trays containing the product were periodically weighed during drying by removing the trays from the atmosphere control unit. Hygroscopic equilibrium was reached when the mass variation of the trays remained constant during three consecutive readings. Equilibrium moisture contents of castor beans for desorption and adsorption processes were determined by gravimetric method in an oven at 105 ± 1 °C, for a 24 h period, in triplicate, according to the seed analysis standard of Brazil (Brasil, 2009).

Thermodynamic parameters, such as entropy of desorption (ΔS), differential enthalpy (ΔH), Gibbs free energy (ΔG) and enthalpy-entropy relationship, were obtained by means of a known methodology, described by Corrêa et al. (2012), and are expressed respectively by Eqs. 1 to 5.

$$\ln a_w = \pm\left(\frac{\Delta H_{st}}{RT} - \frac{\Delta S}{R}\right) \tag{1}$$

$$\Delta H = \Delta H_{st} - \Delta H_{vap} \tag{2}$$

$$\Delta G = \pm RT \cdot \ln a_w \tag{3}$$

$$T_B = \hat{T}_B \pm t_{t_m-2,\alpha/2}\sqrt{\mathrm{Var}\left(T_B\right)} \tag{4}$$

$$T_{hm} = \frac{n_t}{\sum_{i=1}^{n_t}\left(\frac{1}{T_i}\right)} \tag{5}$$

where:

ΔH - isosteric heat of sorption, kJ kg^{-1};

ΔH_{vap} - latent heat of vaporization of pure water, kJ kg^{-1};

ΔH_{st} - net isosteric heat of sorption, kJ kg^{-1};

ΔS - differential entropy of sorption, kJ kg^{-1} K^{-1};

ΔG - Gibbs free energy, kJ kg^{-1} mol^{-1};

T_B - isokinetic temperature, K;

T_{hm} - harmonic mean temperature, K; and,

n_t - number of temperatures utilized.

RESULTS AND DISCUSSION

Figure 1 presents the differential enthalpy of sorption as a function of equilibrium moisture content.

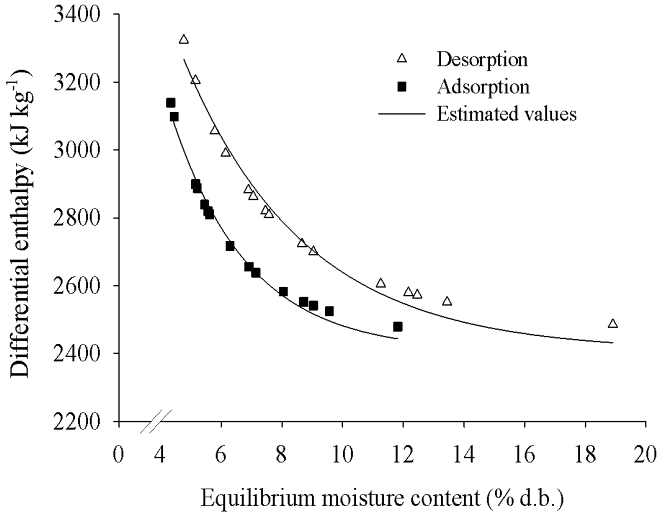

Figure 1. Observed and estimated values of differential enthalpy of sorption as a function of equilibrium moisture content

These values were encountered by adding up the value of latent heat of vaporization of pure water, which represents the lower quantity of energy required to vaporize water. This was calculated at the temperature of 40 °C, which is the mean value of temperature used in this work, resulting in a value of 2406.60 kJ kg^{-1}.

An increase of the energy required to remove water from the product is observed when a reduction of moisture content occurs (Figure 1). This trend is represented by the values of differential enthalpy of desorption. Furthermore, an increase of the energy liberated by water adsorption within the product is noticed, represented by the values of differential enthalpy of adsorption. High values of differential enthalpy of sorption at low values of moisture content may be explained by the differences between bonding forces between water molecules and the adsorbent surface of the product. At initial sorption stages (low values of moisture content), there are polar sorption sites highly active, with elevated interaction energy on the adsorbent surface, which is covered with water molecules, forming a monomolecular layer (Al-Muhtaseb et al., 2004). As water molecules begins to chemically bond with highly active sorption sites, sorption becomes to occur at less active sites (high values of moisture content), with lower interaction energy.

Values of differential enthalpy of sorption are higher than the value of latent heat of vaporization of pure water (Figure 1), indicating that the bonding energy between water molecules and sorption sites is higher than the bonding energy among water molecules in liquid phase (Masuzawa & Sterling, 1968). Furthermore, for both desorption and adsorption, as moisture content increases, values of differential enthalpy of sorption approximate to the value of latent heat of vaporization of pure water. According to Wang & Brennan (1991), the moisture content value at which this approximation occurs is considered to be an indication of free water within the product.

At a constant value of moisture content, values of differential enthalpy of desorption are higher than the values of differential enthalpy of adsorption, as stated previously (Telis et al., 2000; McMinn & Magee, 2003; Kaymak-Ertekin & Gedik, 2004; Goneli et al., 2010a), indicating higher required energy in the desorption process (Kaymak-Ertekin & Gedik, 2004). Higher values of differential enthalpy of desorption indicates that, during desorption, there are more polar sites or sorption sites on adsorbent surface in comparison to the adsorption process (McMinn & Magee, 2003).

The differences between differential enthalpy values of desorption and adsorption are an indication of the hysteresis phenomenon. However, no relationship between hysteresis degree and variation of differential enthalpy values is known (Al-Muhtaseb et al., 2004). According to Telis et al. (2000), a simple explanation for the hysteresis effect on agricultural products is not possible, because the products are a complex combination of several components that can adsorb water independently, but also may interact with each other, providing different water sorption mechanisms.

According to McMinn & Magee (2003), knowledge on differential enthalpy of sorption, at certain moisture content, provides an indication of the state of the water that is sorbed within the product and as a measurement of physical, chemical and biological stability of foodstuffs during storage. Values of differential enthalpy of desorption for castor beans in moisture content range between 4.77 and 18.91% d.b. varied from 3324 to 2486 kJ kg^{-1}, while values of differential enthalpy of adsorption in moisture content range between 4.34 and 11.82% d.b. varied from 3139 to 2479 kJ kg^{-1}. These values are within the range of a previous work with different agricultural products (Goneli et al., 2010a,b). Figure 2 presents values of differential entropy from sorption processes as a function of equilibrium moisture content.

From Figure 2, it is noticed a strong differential entropy dependence upon moisture content, showing a trend similar to that observed for differential enthalpy. Similar results were reported for starch powders (Al-Muhtaseb et al., 2004), bubinga wood (Nkolo Meze'e et al., 2008), okra seeds (Goneli et al., 2010a), pearl millet grain (Goneli et al., 2010b), 'pinhão' seeds (Thys et al., 2010), 'pinhão' flour (Cladera-Olivera et al., 2011), quince fruits (Noshad et al., 2012), coffee fruits (Goneli et al., 2013) and prickly pear seeds (Hessini et al., 2015).

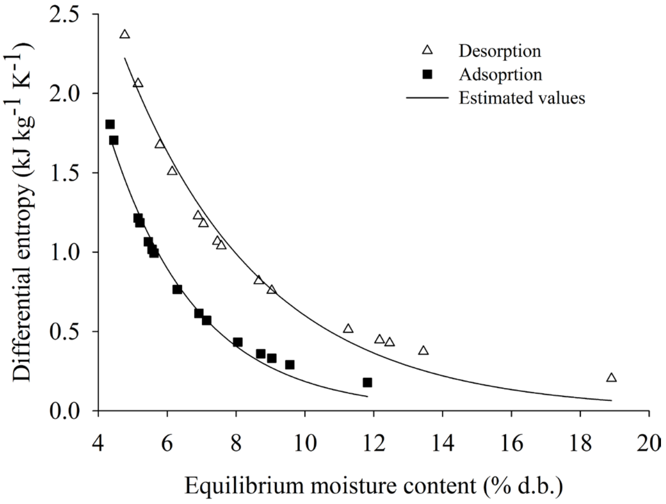

Figure 2. Observed and estimated values of differential entropy of sorption as a function of equilibrium moisture content

According to the second law of thermodynamics, a process is reversible when the sum of all entropy alterations, in each process subsystem, is constant. Thus, desorption and adsorption processes of castor beans are irreversible (hysteresis effect) below 18% (d.b.) of moisture content, since entropy is produced during these processes (Madamba et al., 1996).

Differential entropy values of the desorption process are higher than those from the adsorption process (Figure 2). Differential entropy of a material is proportional to the number of available sorption sites at a specific energy level (Madamba et al., 1996), indicating a mobility state of the water molecules within the product. Thus, results encountered in the present work point that water molecules possess higher mobility during desorption than during adsorption. This trend is in agreement with those found by Al-Muhtaseb et al. (2004) and McMinn & Magge (2003), working with starch powders and potato, respectively. From Figure 2, it is detected that higher values of moisture content lead to a reduction of differential entropy values, tending to remain constant at elevated moisture content value. According to Madamba et al. (1996), these results indicate that, at a certain point of moisture content, the sorption processes can be reversible.

Table 1 presents mathematical models fitted to observed values of differential enthalpy and differential entropy of sorption of castor beans, as a function of equilibrium moisture content. The equations used are satisfactory to describe the phenomenon, presenting elevated values of determination coefficient.

Figure 3 shows the behavior of differential enthalpy values as a function of differential entropy values, for both sorption processes. It was considered that, at a constant value of moisture content, differential enthalpy and entropy are invariant with temperature.

Table 1. Mathematical models fitted to observed data of differential enthalpy of sorption (ΔH, kJ kg^{-1}) and differential entropy of sorption (ΔS, kJ kg^{-1} K^{-1}) as a function of equilibrium moisture content (Xeq, % d.b.) and their respective determination coefficients (R^2)

	Regression equation	R^2 (%)
Desorption	$\Delta H = 2833.33 \exp(-0.2499X_{eq}) + 2406.60$	97.94
	$\Delta S = 7.3155 \exp(-0.2500X_{eq})$	97.94
Adsorption	$\Delta H = 3875.42 \exp(-0.3942X_{eq}) + 2406.60$	98.77
	$\Delta S = 9.5544 \exp(-0.3942X_{eq})$	98.77

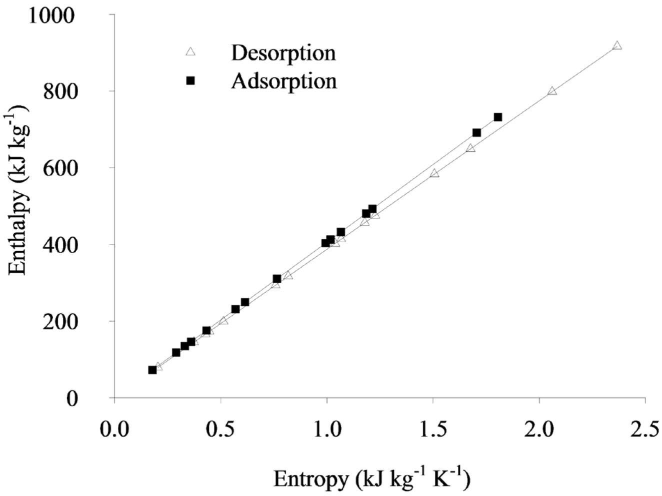

Figure 3. Relationship between differential enthalpy and differential entropy of sorption

Linear relationship for desorption and adsorption processes is observed (Figure 3), with determination coefficient superior to 99%. Due to this high linearity degree between differential enthalpy and differential entropy, the differential enthalpy-entropy compensation theory may be considered valid for the sorption phenomenon in castor beans.

Aiming to test the validity of the differential enthalpy-entropy compensation theory, isokinetic temperature was compared to the mean harmonic temperature from the temperature range used in this work. According to Krug et al. (1976a,b), linear chemical compensation exists if isokinetic temperature is different from the mean harmonic temperature. Isokinetic temperatures for desorption and adsorption processes of castor beans were 387.44 ± 9.72 K and 405.64 ± 10.45 K, respectively. Mean harmonic temperature was 312.76 K, which is different from all isokinetic temperatures found, confirming that the theory is valid for water sorption of castor beans. These values are within the range of previous works with different agricultural products (Goneli et al., 2010b; Cladera-Olivera et al., 2011; Goneli et al, 2013; Hessini et al., 2015).

Isokinetic temperature is the one when all reactions in series occur at the same time, in other words, when the product is in equilibrium. If T_B > Thm, the process is enthalpy controlled; if T_B < Thm, the process is entropy controlled (Leffler, 1955). Thus, water sorption of castor beans is enthalpy controlled. The observed values of Gibbs free energy at isokinetic temperature were -2.55×10^{-4} kJ kg^{-1} and 3.82×10^{-5} kJ kg^{-1}, respectively for desorption and adsorption processes.

Gibbs free energy values related to sorption are presented in Figure 4.

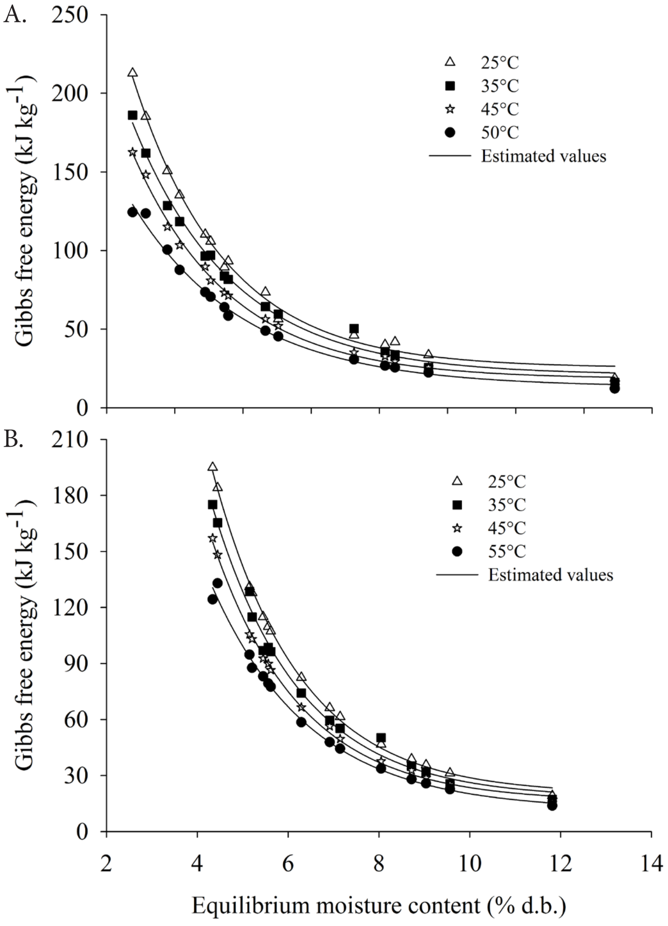

Figure 4. Observed and estimated values of Gibbs free energy for desorption (A) and adsorption (B)

Gibbs free energy is related to the work needed regarding the product layers to become available to sorption (Nkolo Meze'e et al., 2008); therefore, at higher values of equilibrium moisture content, there will be fewer sites available to sorption (Oliveira et al., 2011). Thus, the values presented are expected (Figure 4), because at higher values of moisture content, there is lower necessity of work to make the sites available to sorption, because they are already available. Positive values of this parameter are also expected, as it characterizes endothermic reaction, or else, reactions that require energy from the environment to occur. It can also be noticed that, around 11% of moisture content, castor beans tend to present approximate values for both sorption processes, regardless of the temperature, maintaining this characteristic with increased moisture content.

Table 2 presents mathematical models fitted to observed values of Gibbs free energy related to sorption of castor beans, as a function of equilibrium moisture content. They can be used to predict Gibbs free energy values within the moisture content range between 4 and 20% (d.b.) (for desorption) and between 4 and 12% (d.b.) (for adsorption).

Table 2. Mathematical models of Gibbs free energy (ΔG, kJ kg^{-1}) of castor beans sorption at different temperatures, as a function of equilibrium moisture content (Xeq, % d.b.)

Temperature (°C)	Equation	R^2 (%)
	Desorption	
25	$\Delta G = 25.4358 + 1074.7797 \exp(-0.3692X_{eq})$	99.45
35	$\Delta G = 20.9176 + 808.8154 \exp(-0.3395X_{eq})$	99.09
45	$\Delta G = 18.3900 + 758.5294 \exp(-0.3491X_{eq})$	99.52
55	$\Delta G = 13.2079 + 493.9430 \exp(-0.3038X_{eq})$	99.26
	Adsorption	
25	$\Delta G = 20.0567 + 1689.1809 \exp(-0.5252X_{eq})$	99.87
35	$\Delta G = 18.0211 + 1477.5614 \exp(-0.5184X_{eq})$	99.05
45	$\Delta G = 16.1572 + 1311.1835 \exp(-0.5175X_{eq})$	99.79
55	$\Delta G = 11.5451 + 882.7756 \exp(-0.4615X_{eq})$	97.22

CONCLUSIONS

1. Differential enthalpy, differential entropy and Gibbs free energy presented high correlation with the equilibrium moisture content of castor beans, in which these properties increased as moisture content decreased.

2. Differential enthalpy of desorption and adsorption varied from 3324 to 2486 kJ kg^{-1} and from 3139 to 2479 kJ kg^{-1}, respectively.

3. The enthalpy–entropy compensation theory exists for the sorption process of castor beans, being enthalpy controlled.

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