Thermodynamic Analysis of Cinnamon Sorption Isotherms
(Cinnamomum zeylanicum)

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ABSTRACT
Sorption isotherms of cinnamon were determined to 20, 30 and 40°C, within a water activity (aw) range of 0.11 to 0.99. The isotherms obtained are type II sigmoid shape. The equilibrium moisture content decreased with increasing temperature to a constant water activity. The monolayer moisture content decreased when temperature increase; its content on dry basis was 6.27, 5.33, 4.77% at 20, 30 and 40°C. Both the isosteric heat of sorption as the system entropy decreased when temperature and equilibrium moisture content increased. The moisture sorption process of cinnamon was less spontaneous as increases temperature and the equilibrium moisture content. Of the nine models tested, the GAB and Henderson models fit better with the experimental sorption isotherms of cinnamon in both ranges of aw and the different temperatures; while the models of BET, Smith, Caurie, Kuhn, and Oswin, had good fit with the experimental sorption isotherms of cinnamon, only in the range of aw from 0.1 to 0.5. The cinnamon should be stored at 25°C and at a moisture content of 5.33%, in order to achieve its longer shelf life.

Key words: cinnamon, sorption, isotherms, modeling, thermodynamic properties.

INTRODUCTION
Cinnamon is among the oldest spices known and used by man, is obtained from many species of the genus Cinnamomum, belonging to Lauraceae family. In this genus about 250 species, which are grown intensively in Sri Lanka, southern India, China, Burma and Indonesia as well as in the Seychelles, Madagascar and Brazil islands, places of hot and humid weather [1,2]. The species of higher economic value are C. cassia, C. zeylanicum, C. tamala, C. pauciflorum, and C. burmannii; which is due to both its culinary and therapeutic properties and they have been widely used in traditional medicine of their origin country [3].

Cinnamon has been used in many countries since ancient times to treat dyspepsia, gastritis, inflammatory diseases, and circulatory disorders [4]; also present antiallergic, antiulcerogenic, antipyretic, analgesic and anesthetic properties [5]. Due to its high concentration of phenolic compounds, cinnamon is regarded as one of the foods with the highest antioxidant capacity, which makes it an excellent functional food [1]. It has been observed that cinnamon extracts inhibit the action of α-glucosidase and α-amylase enzymes, which is a therapeutic ways to slow digestion and absorption of carbohydrates and, consequently, reducing postprandial blood glucose, so consumption of this species represents an alternative for the early stages of hyperglycemia in diabetes [6].

The most important constituents of cinnamon are in its essential oil, which is integrated by (trans-cinnamaldehyde, 3-methoxy-1,2-propanediol, eugenol and 5-(2-propenyl)-1,3-benzodioxol) [7], as well as cinnamyl acetate and caryophyllene which have special characteristics of aroma and flavor, so they are
highly demanded by food, pharmaceutical and perfumery industries [1]. The cinnamon essential oil has also been used in the preparation of edible biodegradable films, in combination with isolated soy protein and sodium caseinate [8]. Has also shown that these oils have excellent antibacterial, antifungal, antitermite and anti-mosquito activity [9, 10]. In vitro studies has been proved that cinnamon extracts mimic the function of insulin, thereby improving the action of this hormone in isolated adipocytes [11]. The cinnamon extract can also enhance the function of the insulin receptor [12].

Despite the economic importance of cinnamon, there is not studies on the thermodynamic parameters and monolayer humidity required for better handling during distribution and storage and thus preserve all its nutritional and functional properties. The aim of this work consisted to make the sorption isotherms of the cinnamon powder and determine its physicochemical parameters during storage under different conditions of humidity and temperature in order to establish optimal storage conditions.

MATERIALS AND METHODS
Proximal Analyses
Moisture, ash, protein (N×6.25), fat and crude fiber contents were determined according to standard methods[13], and total carbohydrates content was determined by difference.

Cinnamon granulometry
The determination of the cinnamon particle size was performed according to the methodology proposed by Bedolla and Rooney [14]. For this was used a Sieve Shaker Model SS-3 (WS TYLER®, USA), equipped with 6 sieves of 3 inches in diameter and mesh numbers of: 50, 70, 100, 140, 200, and 400. Samples of 100g of cinnamon powder were placed in the sieving machine for 15 minutes. At the end of the sieving time, cinnamon fractions retained on each sieve were collected and weighed, to determine the percentage of powder retained on each sieve.

Determination of the sorption isotherms
Initially the cinnamon powder was placed in a vacuum drying oven model EV-50 (RAYPA. Germany), equipped with temperature control and drying time. Drying was carried out at 60 °C to constant weight. The sorption isotherms of the cinnamon powder were determined according with Wink method [15], which is a gravimetric method and is as follow: Cinnamon samples whose moisture content is known, are exposed in an atmosphere whose relative humidity is also known, until equilibrium is reached. To do this, the trays that will contain the material to be analyzed, were washed, drained and dried at 100°C in an Arsa oven with digital display of temperature, to reach their weight constant and then were placed in a desiccator to prevent moisture pickup. The weight of empty trays were registered and about 1.0000 g cinnamon powder previously dried was added. The sample weight was obtained by difference and the trays were placed in the desiccator to prevent moisture pickup. The weight of empty trays were registered and about 1.0000 g cinnamon powder previously dried was added.

Three sets of 10 cameras each were used with different saturated salt solutions, covering a range of water activities from 0.1123 to 0.9877. The first set of 10 cameras was placed at laboratory temperature (20±2°C), the second set were placed at 30±1°C in an Arsa oven with digital display of temperature, model AR-290D (Manufacturers Feligneo, SA de CV, Mexico), to reach their weight constant and then were placed in a desiccator to prevent moisture pickup. The weight of empty trays were registered and about 1.0000 g cinnamon powder previously dried was added. Then the trays were exposed in an atmosphere whose relative humidity is also known, until equilibrium is reached.

Determination of thermodynamic parameters
Humidity monolayer
The moisture content of monolayer of cinnamon powder was determined by applying the model developed by Stephen Brunauer, Paul Emmett and Edward Teller from the Langmuir isotherm, and better known as the BET model, which states that:

\[
\frac{a_w}{(1-a_w)X} = \frac{a_w(C-1)}{XoC} + \frac{1}{XoC} \ldots (1)
\]

where: \(a_w\) = water activity; \(X\) = moisture content to any water activity; \(C\) = Constant related to the binding energy and \(Xo\) = moisture content of monolayer.
The BET equation can be rewritten as [17]:

\[
\frac{1}{(1 - a_w)X} = \alpha + \beta a_w \quad \ldots (2)
\]

Considering that:

\[
X_a = \frac{1}{\alpha + \beta} \quad \ldots (3) \quad \text{and} \quad C = \frac{\alpha + \beta}{\alpha} \quad \ldots (4)
\]

**Isosteric heat of sorption**

The isosteric heat of sorption or differential enthalpy is defined as the energy required to change a unit mass of a product of liquid state to vapor, at a temperature and water activity determined [18]; while that the net isosteric heat of sorption \( (Q_s) \) is defined as the isosteric heat of sorption of food \( (\Delta H) \) minus the latent heat of vaporization of pure water \( (\Delta H_v) \), and they can be obtained from the sorption isotherm of experimental data from the Clausius-Clapeyron[19].

\[
\ln a_w = -\frac{\Delta H}{R} \left(\frac{1}{T}\right) + C \quad \ldots (5); \quad Q_s = \Delta H - \Delta H_v \quad \ldots (6)
\]

where: \( \Delta H \)=isosteric heat of sorption or differential enthalpy (cal / mol); \( Q_s = \)net isosteric heat of sorption (cal / mol); \( R \)=universal gas constant (1.9872 cal / mol K). \( T \)=temperature at which the study was conducted (K); \( \Delta H_v \)=latent heat of vaporization of pure water, whose values at different temperatures are: -10553, -10454 and -10350 calories/mol at temperature of 20, 30 and 40°C respectively.

**The Gibbs free energy**

The Gibbs free energy for the water adsorption of the cinnamon at different temperatures, is defined by the following equation:

\[
\Delta G = RT \ln a_w \quad \ldots (7)
\]

where: \( \Delta G \)=Gibbs free energy; \( R \)=universal gas constant (calories / mol K); \( a_w \)=water activity and \( T \)=temperature (K).

**Sorption Entropy**

The water sorption entropy \( (\Delta S) \) is defined by the following equation:

\[
\Delta S = \frac{\Delta H - \Delta G}{T} \quad \ldots (8)
\]

**Modeling sorption isotherms**

In order to determine the best mathematical model for predicting the performance of sorption of the cinnamon, the experimentally obtained data was applied to nine different equations isotherms, which were: GAB (Guggenheim, Anderson and de Boer), BET (Brunauer, Emmett and Teller), Henderson, Caurie, Oswin, Iglesias-cherife, Khun, Smith and Bradley [20].

The quality of the fit between the experimental data \( (X_e) \) and the data obtained with the different proposed models \( (X_c) \) was assessed using linear correlation coefficient \( (R^2) \) and the percentage standard error \( (E\%) \), which was calculated according to the following equation (Eq. 9).

\[
E\% = \frac{100}{n} \sum_{i=1}^{n} \left(\frac{X_e - X_c}{X_e}\right) \quad \ldots (9)
\]

**RESULTS AND DISCUSSION**

The percentage chemical composition of the cinnamon is presented in Table 1. The low moisture content in cinnamon promotes its conservation for long periods during storage, transport, distribution and marketing. On a dry basis, the crude fiber is the main constituent of cinnamon and this is classified as a functional food ingredient [21]. Because cinnamon is consumed mainly as flavoring and flavoring through infusions, candies and desserts, the quantities of cinnamon ingested are minimal and thus its contribution to diet with fiber and others constituent is negligible.

<table>
<thead>
<tr>
<th>Component</th>
<th>Content (%)</th>
<th>DB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Humidity</td>
<td>9.85 ± 0.20</td>
<td></td>
</tr>
<tr>
<td>Ashes</td>
<td>4.60 ± 0.11</td>
<td></td>
</tr>
<tr>
<td>Protein</td>
<td>4.05 ± 0.13</td>
<td></td>
</tr>
<tr>
<td>Crude fiber</td>
<td>3.61 ± 0.15</td>
<td></td>
</tr>
<tr>
<td>Ethereal extract</td>
<td>60.53 ± 0.35</td>
<td></td>
</tr>
<tr>
<td>Total carbohydrates</td>
<td>27.21 ± 0.19</td>
<td></td>
</tr>
</tbody>
</table>

**Cinnamon granulometry**

The 32.80% of the cinnamon powder particles had a mean size of between 37 to 75 µm, while the 84.89% of particles were retained in the mesh No. 400; i.e. its average size was greater than 37 µm and only
15.11% of the particles were able to pass through the mesh No. 400; that is, its average size was less than 37 µm (Table 2). Andrieu et al., [22] found that the particle size distribution in the semolina had no significant effect on the isotherm, moreover, Hebrard et al., [23] mention that the particle size of the semolina did not affect the amount of water absorbed, but if affects the adsorption rate. It has been reported that the monolayer moisture content was independent of the particle size in the semolina and wheat flour [16].

Table 2. Granulometric profile of cinnamon

<table>
<thead>
<tr>
<th>Mesh N°</th>
<th>Sieve opening (µm)</th>
<th>Retention (%)</th>
<th>Cumulative retention (%)</th>
<th>Through Hole (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>300</td>
<td>2.86 ± 0.08</td>
<td>2.86 ± 0.08</td>
<td>97.14 ± 0.08</td>
</tr>
<tr>
<td>70</td>
<td>212</td>
<td>3.28 ± 0.10</td>
<td>6.14 ± 0.09</td>
<td>93.86 ± 0.09</td>
</tr>
<tr>
<td>100</td>
<td>150</td>
<td>7.85 ± 0.15</td>
<td>13.99 ± 0.11</td>
<td>86.01 ± 0.11</td>
</tr>
<tr>
<td>140</td>
<td>106</td>
<td>12.71 ± 0.18</td>
<td>26.70 ± 0.13</td>
<td>73.30 ± 0.13</td>
</tr>
<tr>
<td>200</td>
<td>75</td>
<td>25.39 ± 0.20</td>
<td>52.09 ± 0.14</td>
<td>47.91 ± 0.14</td>
</tr>
<tr>
<td>400</td>
<td>37</td>
<td>32.80 ± 0.22</td>
<td>84.89 ± 0.16</td>
<td>15.11 ± 0.16</td>
</tr>
<tr>
<td>Bottom</td>
<td></td>
<td>15.11 ± 0.16</td>
<td>100.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Sorption isotherms

Sorption isotherms show that both the equilibrium moisture content and water activity were significantly affected (p<0.05) by temperature. The equilibrium moisture content increases with decreasing temperature to the same aw, or, aw increases when temperature increases to the same equilibrium moisture content (Figure 1).

Figure 1. Sorption isotherms of cinnamon at different temperatures

These isotherms show a sigmoid curve which corresponds to a type II isotherm [24], integrated by three distinct zones which reflect how water molecules bind to the food components [25]. The first zone covers an aw between 0.1-0.2 and represents the water molecules strongly attached to the food components; the second zone covers an interval of aw between 0.6-0.7 and comprising the water molecules that it is present in small capillaries and can be regarded as the continuous transition between bound water and free water, its bond forces are less than the water bound in the first zone. The third zone of the isotherm covers aw> 0.7 and comprising water involved in filling the large pores and the solutes dissolution. The properties of the water in this area are similar to those of free water [26]. This type of isotherms are present most often in foodstuffs and are due to the formation of multiple layers [27]. Cinnamon powder absorbs more water at low temperatures because that at these temperatures, water molecules have lower kinetic energy that is insufficient to overcome the corresponding sorption energy.
Another possible explanation for this phenomenon is that the water molecules are attached through links by hydrogen bonds to the polar sites of the food components, such as starch, proteins and cellulose, and since formation of these links by hydrogen bond is an exothermic reaction, is possible that a temperature increase produces the decrease these reactions, so that water binding of to the food components also decreases [16]. Furthermore, the fact that a constant aw decrease the moisture content equilibrium when temperature increases, shows that the cinnamon powder becomes less hygroscopic due to the reduction of total number of active sites for binding of water molecules, as a result of the physical or chemical changes in the product, caused by the increase in temperature [20].

The adjust of the sorption isotherms with the BET model, was carried out by the method of linear regression, an graphical representation of aw / (1 - aw)X vs. aw, was made within a range equilibrium moisture corresponding to an aw of 0.1 to 0.5 for the different temperatures, and the equations of the corresponding lines are obtained, as well as the correlation coefficient and the monolayer moisture (Table 3). The BET model fits well with the experimental isotherm data of cinnamon, since in all cases, the correlation coefficient R² of the lines obtained was greater than 0.98 in the three different working temperatures, because of that, the BET model equations can be used to predict the cinnamon sorption isotherms, within a range of aw between 0.1 to 0.5, corresponding to a moisture content of 0.02 to 0.12 g H₂O / g dry solid. By interpolating the values of monolayer moisture content in the respective sorption isotherm, or in the BET equation model, the aw corresponding with this value of monolayer moisture was obtained and in this case it was of 0.2 to 0.25.

Table 3. Thermodynamic constants for cinnamon obtained by BET model

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Line's Equation</th>
<th>R²</th>
<th>(Xo)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>Y = 0.1395X + 0.0201</td>
<td>0.9973</td>
<td>6.27</td>
</tr>
<tr>
<td>303</td>
<td>Y = 0.1652X + 0.0223</td>
<td>0.9912</td>
<td>5.33</td>
</tr>
<tr>
<td>313</td>
<td>Y = 0.1789X + 0.0308</td>
<td>0.9839</td>
<td>4.77</td>
</tr>
</tbody>
</table>

Xo = monolayer moisture content (g H₂O / 100 g dry solid)

Similarly with the equilibrium moisture content, monolayer moisture content (Xo) of cinnamon decreased with increasing temperature, which may be due to a reduction in the total number of active sites for attachment of water as a result of physical and/or chemical changes in the product, which are induced by temperature [28]. Another possible explanation could be that as temperature increases, water molecules are energized due to an increased energy level, causing the breaking of the binding sites of the water molecules with food components, decreasing thus the moisture content of monolayer [29].

The monolayer humidity value (Xo) indicates the moisture content where food is most stable, since it is the point where the most chemical reactions are performed at lower speeds and in which there is no growth of microorganisms, given that do not have water available to it; by other hand, moisture contents below the monolayer, promote oxidation reactions of fatty acids, causing the foods rancidity [30].

The importance to know the monolayer moisture content of a food is that we can keep their chemical, biochemical and organoleptic properties and therefore extend their shelf life, if we maintain the food to a moisture content corresponding to the monolayer humidity. Erbas et al., [16] state that the monolayer moisture content is an important parameter for to storage and food spoilage, and it is considered as the sorption water capacity of the adsorbent and as an indicator of available polar sites for binding steam. Meanwhile, Chirife and Iglesias [28] mention that the concept of monolayer is useful because of its relation to various aspects of physical and chemical degradation of dry products.

The net isosteric heat of sorption (Qs) is a direct function of the temperature and the moisture adsorption capacity of food, is indicative of the intermolecular attractive forces between the adsorption sites and water vapor [31]. The heat of sorption is highly dependent on moisture content, it decreases when equilibrium moisture content increase and also with increasing temperature (Figure 2).
The net isosteric heat of sorption reflects the different energy required for binding water, initially to the highly active polar sites present on the surface of the constituents of cinnamon, which require greater interaction energy, followed by the progressive filling of the less available sites requiring lower activation energies. In our case study, the net isosteric heat of sorption decreased from 13.049 to 12.051; of 12.799 to 11.801 and from 12.589 to 11.592 calories/mole, when the moisture content increased from 2 to 14 g of H₂O/100 g dry solids and the working temperature was set at 20, 30 and 40 °C respectively. It can also be seen that as moisture content increases, the net isosteric heat of sorption decreases and tends to be equal to the pure water having in each of the different temperatures selected, indicating that moisture existing in the food in these conditions, is already as free water [32].

The net isosteric heat of sorption corresponding to a specific moisture content, it indicates the amount of adsorbed water and thus is a measure of the physical, chemical and microbiological stability of food under the storage conditions applied. McMinn and Magee [31] mentioned that the variation in the heat of sorption with moisture content and relative magnitude of the latent heat of vaporization of pure water, provides valuable data for energy consumption calculation and drying equipment design.

Gibbs free energy (ΔG) at a given temperature, provides a criterion to judge whether the absorption of water by the cinnamon is a spontaneous process (ΔG acquires negative values) or not (ΔG takes positive values) [17]. The Gibbs free energy was less negative as the equilibrium moisture content is increased (Fig. 3), which means that the phenomenon of moisture adsorption by the cinnamon is less spontaneous as its moisture content increases.
The Gibbs free energy is also less negative when temperature increasing, but independently thereof, the moisture sorption process for the cinnamon is a process that takes place spontaneously at the different operating temperatures and within the moisture content range studied (2-14%), as in all cases, the Gibbs free energy had negative values.

The system's entropy shows an inverse dependence with the equilibrium moisture content and temperature (Figure 4), and it is consistent with that reported by other researchers [33]; It has a similar exponential trend to that shows the isosteric heat of sorption; that is, the system entropy decreases with increasing moisture content in the cinnamon, and also with increasing the temperature. This behavior has also been observed in products such as carrots [34] and seeds of lemon [35], tapioca [17]. McMinn and Magee [31] considered that in the range of low water activity, the decrease in the values of the differential entropy of the system is possibly caused by the sites stronger bond between water molecules and solid constituents of food.

![Figure 4. Entropy sorption of cinnamon with the equilibrium moisture content and temperature](image)

In order to determine the best model to predict the behavior of the phenomenon of water sorption of the cinnamon, experimental sorption data were applied in nine different sorption equations, selecting those model that had the lowest deviation; the obtained results at three different temperatures, and in both intervals of aw selected, they are presented in Table 4.

It has been reported that for practical purposes, those mathematical models whose E% is less than 10%, representing a good alternative for predicting the water sorption phenomenon in the product studied [36]. In this context, GAB and Henderson models did have a better fit with the experimental sorption isotherms of cinnamon, within two aw intervals and the three different working temperatures; although the GAB model had lower values of E% in all conditions studied. The Chirife-Iglesias model had an E% > 10% only in the range of aw from 0.5 - 1.0, and temperature of 40°C. Moreover, the BET, Smith, Caurie, Kuh, and Oswin models; all of them had an E% < 10% within the range of aw from 0.1 to 0.5 and at the three different working temperatures, while Bradley model provided a good fit (E% < 10%) in both aw intervals but only at temperatures of 30 and 40°C. Sopade and Ajisegeri [37] mention that the Henderson model is best suited to describe the behavior of moisture sorption by starchy foods. Moreira et al., [38] mention that is not convenient to do comparison of the thermodynamic parameters of different food products obtained from its sorption isotherms, because each one of them is constituted by a complex combination of several components, which not only adsorb water independently but can also interact with each other, hence the thermodynamic parameters are specific to each type of food and under the established work conditions.

According to the obtained information, we can say that to achieve greater stability in the preservation of their physical, chemical, organoleptic and functional properties, the cinnamon powder should be stored at a moisture content of 5.33 g H₂O / 100 g dry solid, and at temperatures of 25°C, because under these conditions, cinnamon have a longer shelf life.
CONCLUSIONS
The moisture sorption isotherms of cinnamon show sigmoidal shape and correspond to type II, according to BET classification. The water sorption capacity of the cinnamon decreased with increasing temperature at a constant water activity, indicating that the moisture adsorption process is an exothermic reaction. The monolayer moisture decreased with increasing temperature, its dry basis content was 6.27, 5.33, and 4.77% at temperatures of 20, 30 and 40°C, respectively, and water activity from 0.2 to 0.25. Both the isosteric heat of sorption as the system entropy, decreased with increasing temperature and the equilibrium moisture content. The isosteric heat of sorption tends to reach the latent heat of vaporization of pure water, with increasing equilibrium moisture content. The moisture sorption process of the cinnamon powder becomes less spontaneous as the temperature and the equilibrium moisture content increased, which is reflected in the Gibbs free energy value. GAB and Henderson models fit better with the experimental sorption isotherms of cinnamon in both ranges of water activities and moisture content was 6.27, 5.33, and 4.77% at temperatures of 20, 30 and 40°C, respectively.

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