ABSTRACT - The aim of this study was to model and determine the thermodynamic properties of moisture sorption in soursop fruit powder. The isotherms were determined by the static method at temperatures of 10, 20, 30, 40 and 50 °C, and a water activity of between 0.113 and 0.868 (decimal). The GAB model effectively described the moisture sorption phenomenon of soursop powder. The monolayer moisture content ranged from 12.589 to 9.109% db. The enthalpy values related to the GAB model were negative, with $-2581.035 \text{kJ kg}^{-1}$ for $C_0$ and $-107,758 \text{kJ kg}^{-1}$ for $K_0$. The isosteric heat of sorption, entropy and Gibbs free energy had a high correlation with the equilibrium moisture content, and the correlation between enthalpy and entropy was confirmed for moisture sorption in soursop powder.

Key words: Monolayer. Entropy. Gibbs free energy. Annona muricata L.

RESUMO - Objetivou-se modelar e determinar as propriedades termodinâmicas de sorção de água em pó de graviola. As isotermas foram determinadas pelo método estático nas temperaturas de 10; 20; 30; 40 e 50 °C e atividade de água entre 0,113 a 0,868 (decimal). O modelo de GAB descreveu bem o fenômeno de sorção de água do pó de graviola. O teor de água da monocamada variou de 12,589 a 9,109% b.s. Os valores de entalpia relacionados ao modelo de GAB foram negativos, com valor de $-2581.035 \text{kJ kg}^{-1}$ para $C_0$ e $-107,758 \text{kJ kg}^{-1}$ para $K_0$. O calor isostérico de sorção, a entropia e a energia livre de Gibbs apresentaram alta correlação com o teor de água de equilíbrio e a correlação entalpia e entropia se confirmou para a sorção de água em pó de graviola.


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INTRODUCTION

Dehydrated foods tend to gain water from the storage environment, thereby altering their water activity until equilibrium is again restored. Alterations in powdered foods include agglomeration, changes in texture, a change in colour and even microbial growth, with such changes tending to lead to rejection of the product (MEDEIROS; LANNES, 2010). To better understand and control the factors affecting food stability, there exists a tool known as the hygroscopic equilibrium curve or sorption isotherm.

Sorption isotherms are curves that relate the moisture content of a product to the equilibrium water activity for any given temperature. According to Damodaran, Parkin and Fennema (2010), information derived from these curves is useful for studying and controlling the processes of preservation and dehydration, for formulating food mixtures to prevent water transfer between the ingredients, for determining the necessary water-barrier properties of the packaging material, for ascertaining the water content that will reduce the growth of microorganisms of interest in a system, and for predicting the physical and chemical stability of foods as a result of changes in their water content.

According to Corrêa, Oliveira and Santos (2012), using thermodynamic properties, it is possible to calculate the energy demands of a process, investigate the properties of the adsorbed water, evaluate microstructures, and evaluate the physical phenomena that occur on the surface of the food.

Thermodynamic parameters such as enthalpy, entropy, Gibbs free energy, isosteric heat and others have been investigated for rhizome starch in Hedychium coronarium (ASCHERI et al., 2009), mango powders (CANO-HIGUITA et al., 2015), lyophilised mango-pulp powder (MOREIRA et al., 2013), red pepper (KALEEMULLAH; KAILAPPAN, 2007) and green coconut pulp (LAVOYER et al., 2013). There are, however, no studies of soursop powder. As such, the aim here was to fit the GAB model and determine the thermodynamic properties of moisture sorption in soursop fruit powder.

MATERIAL AND METHODS

Soursop powder was obtained by foam drying the fruit pulp. For this, 7.43% by weight albumin was added to the pulp, whose mean moisture content was 43.08% db (4.301 kg w kg dm$^{-1}$), and mixed in a domestic mixer for 15 min. The foam was then spread on trays and dried in a forced air circulation oven at 60 °C at a mean air velocity of 5.6 m s$^{-1}$. The resulting powder, with a mean moisture content of 18.12% db, was used to obtain the equilibrium moisture content by means of the static method, employing BOD chambers kept at temperatures of 10, 20, 30, 40 and 50 °C, and a desiccator with saturated solutions whose water activity values are shown in Table 1.

Samples containing approximately 4 g of product were used for each test, with five replications. During the sorption process, the samples were weighed periodically until the weight variation over three consecutive readings was equal to or less than 0.001 g, representing the hygroscopic equilibrium moisture content at that time.

The GAB model was fitted to the observed data for hygroscopic equilibrium using the following Equation:

$$X_e = \frac{X_m \alpha}{[1 - \alpha]^{\alpha} - \alpha(\alpha_e)}$$

where: $X_e$: equilibrium moisture content, % db; $X_m$: monolayer moisture content, % db; aw: water activity, decimal; C and $\kappa$: parameters of the GAB model related to the monolayer and multilayer properties respectively, dimensionless.

The experimental data for the moisture sorption of soursop powder were subjected to nonlinear regression analysis by the Gauss-Newton method using the Statistic 7.0® software (STATSOFT, 2004).

To analyse the goodness of fit of the model, the magnitude of the coefficient of determination, the mean relative error (P) (Equation 2), the estimated mean error (SE) (Equation 3) and the residual distribution (RD) were considered.

$$P = \frac{\sum_{i=1}^{n} (\frac{\hat{Y}_i - Y_i}{Y_i})}{n}$$

$$SE = \frac{\sum_{i=1}^{n} (\hat{Y}_i - Y_i)^2}{DF}$$

where: $Y_i$: observed value; $\hat{Y}_i$: estimated value; n: number of observed data; DF: degrees of freedom.

After obtaining the coefficients of the GAB model, the enthalpy values associated with the variation in each coefficient with temperature were calculated by a graphic representation of ln($X_m$), ln(C) and ln($\kappa$) vs. the inverse of the absolute temperature ($T_a^{-1}$).

$$C = C_0 \exp\left(\frac{\Delta H_1}{R T_a}\right)$$

$$K = K_0 \exp\left(\frac{\Delta H_2}{R T_a}\right)$$

$$X_e = X_{eq} \exp\left(\frac{\Delta H_3}{R T_a}\right)$$

where: $X_{eq}$: pre-exponential factor, % db; $C_0$ and $K_0$: pre-exponential factors, dimensionless; $\Delta H_1$, $\Delta H_2$ and $\Delta H_3$;
Table 1 - Water activity of the saturated solutions at different temperatures

<table>
<thead>
<tr>
<th>Chemical Compound</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10</td>
</tr>
<tr>
<td>LiCl</td>
<td>0.113</td>
</tr>
<tr>
<td>MgCl₂·6H₂O</td>
<td>0.335</td>
</tr>
<tr>
<td>NaBr</td>
<td>0.622</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.757</td>
</tr>
<tr>
<td>KCl</td>
<td>0.868</td>
</tr>
</tbody>
</table>

Increments in enthalpy associated with the variation in GAB model parameters with temperature, kJ mol⁻¹; R: universal gas constant, 8.314 J mol⁻¹ K⁻¹; T: absolute temperature, K.

The isosteric heat of sorption was calculated from the Clausius-Clayperon equation (IGLESIAS; CHIRIFE, 1976).

\[ \frac{\partial \ln \alpha}{\partial T} = \frac{\Delta h_{st}}{R T^2} \]  

where: \( \Delta h_{st} \): net isosteric heat of sorption or differential enthalpy, kJ kg⁻¹.

Integrating Equation 7, and assuming the net heat of sorption to be independent of temperature for each value of equilibrium moisture content, the following equation (Equation 8) is obtained (WANG; BRENNAN, 1991):

\[ \ln \alpha = \left( \frac{\Delta h_{st}}{R T^2} \right) + C_1 \]  

where: \( C_1 \): constant of integration, dimensionless.

The integral isosteric heat of sorption was obtained by adding to the values for net isosteric heat of sorption, the value for the latent heat of vaporisation of free water, as per Equation 9:

\[ Q_w = \Delta h_w + L \]  

where: \( L \): latent heat of vaporisation of free water, kJ kg⁻¹; \( Q_w \): Integral isosteric heat of sorption, kJ kg⁻¹.

The latent heat of vaporisation of free water required to calculate the integral isosteric heat of sorption was obtained from the mean temperature (\( \bar{T} \)) for the range under study, in °C, as shown in Equation 10 (OLIVEIRA et al., 2011):

\[ L = 2502.2 - 2.39 \bar{T} \]  

Changes in the differential entropy of sorption were calculated using the Gibbs-Helmholtz equation (RIZVI, 1995):

\[ \Delta S = \frac{\Delta h_w - \Delta G}{T} \]  

where: \( \Delta S \): differential entropy of sorption, kJ kg⁻¹ K⁻¹; \( \Delta G \): Gibbs free energy, kJ kg⁻¹.

The Gibbs free energy was calculated with the following equation:

\[ \Delta G = \pm R T \ln(\alpha) \]  

The effect of changes in moisture sorption on free energy is generally also accompanied by changes in enthalpy and entropy values. As such, substituting Equation 12 into Equation 11, and rearranging:

\[ \ln(\alpha) = \frac{\Delta h_{st} - \Delta S}{R} \]  

The net isosteric heat of sorption and entropy were calculated with Equation 13, plotting the values of water activity against \( T^{-1} \) at the respective values of the equilibrium moisture content.

The values calculated for the differential enthalpy of sorption and entropy were related using Equation 14 (BERISTAIN; GARCIA; AZUARA, 1996):

\[ \Delta h_{st} = T_w (\Delta S) + \Delta G_{st} \]  

where: \( T_w \): isokinetic temperature, K; \( \Delta G_{st} \): Gibbs free energy at the isokinetic temperature, kJ kg⁻¹.

To confirm the existence of the compensation theory, the isokinetic temperature was compared to the harmonic mean temperature, defined as per Equation 15 (KRUG; HUNTER; GRIEGER, 1976a, b):

\[ T_{hm} = \frac{1}{\frac{1}{T_1} + \frac{1}{T_2} + \frac{1}{T_n}} \]  

where: \( T_{hm} \): harmonic mean temperature, K; \( n \): number of temperatures used.

According to Krug, Hunter and Grieager (1976a, b), linear chemical compensation only exists if the isokinetic temperature (TB) is different from the harmonic mean temperature (T_{hm}).
An approximate confidence interval, $(1-\alpha) 100\%$, for the isokinetic temperature can be calculated with the following equation:

$$T_k = T_0 \pm t_{1-\alpha/2, \chi^2} \sqrt{\text{Var}(T_0)}$$

where:

$$t_{1-\alpha/2, \chi^2} = \sum \left( \Delta H - \Delta H_k \Delta S - \Delta S_k \right) \sum (\Delta S - \Delta S_k)^2$$

and

$$\text{Var}(T_0) = \sum \left( \Delta H - \Delta H_k \Delta S - \Delta S_k \right)^2$$

where: $m$: number of data pairs for enthalpy and entropy; $\Delta H$: mean value for enthalpy, kJ kg$^{-1}$; $\Delta S$: mean value for entropy, kJ kg$^{-1}$ K$^{-1}$.

**RESULTS AND DISCUSSION**

Table 2 shows the values of the relative mean error, estimated mean error, coefficients of determination and residual distribution of the GAB model for the hygroscopic equilibrium moisture content of the soursop powder, at a temperature range of 10 to 50 °C. A good fit can be seen for the model.

The coefficient of determination, despite not being a good parameter for verifying the fit of nonlinear models, generally has higher values or the model that better fit the experimental data (RESENDE et al., 2010). The coefficients of determination were greater than 99% for each temperature under study.

The estimated mean error (SE), which describes the estimated value of the standard deviation, had lower values under all conditions, and as such, the model can be used to represent the phenomenon. It is worth noting that the lower the value for SE, the better the goodness of fit of the model relative to the observed data. It is known that the ability of a model to accurately describe a given physical process is inversely proportional to the value of the estimated mean error.

According to Henao, Queiroz and Haj-Isa (2009), Rosa, Moraes and Pinto (2010), Corrêa et al. (2014), and Costa et al. (2015), values below 10% for the relative mean error indicate high suitability for practical purposes; therefore, analysing the values obtained, it can be seen that the GAB model is suitable for describing the phenomenon of moisture sorption in soursop powder.

Finally, an analysis of the residual distribution is necessary for a correct evaluation of the model. Even when the statistical parameters show good results, the model can be ineffective if it presents a biased residual distribution (OLIVEIRA et al., 2017a). This was not seen.

Application of the GAB model is more advantageous than other models, as its coefficients show physical significance, allowing a more detailed study of the heat and mass transfer that occur during sorption. In addition, it is suitable for describing experimental data up to a water activity of 0.90 (OLIVEIRA et al., 2011, 2017b).

The GAB model also satisfactorily fitted the isotherms of the powder from the coité and espada varieties of mango (BEZERRA et al., 2010), and from the Rosa and Tommy Atkins varieties (BEZERRA et al., 2011), of the parts, skin, pulp and fibre from fruits of the buriti (Mauritia flexuosa) (MELO et al., 2011), and of lyophilised mango powder (MOREIRA et al., 2013).

According to Oliveira et al. (2011), the moisture content of the monolayer indicates high moisture sorption at specific sites in the food; this value must be reached in order to ensure the stability of the food (LAVOYER et al., 2013). Values for this coefficient decreased as the temperature increased (Table 2), ranging from 12.589 to 9.109% db. In the literature, this phenomenon has been attributed to a reduction in the number of active sites with an increase in temperature (PERDOMO et al., 2009).

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>P (%)</th>
<th>SE</th>
<th>R² (%)</th>
<th>DR</th>
<th>Estimated parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Xₘ (% db)</td>
</tr>
<tr>
<td>10 °C</td>
<td>3.602</td>
<td>1.770</td>
<td>99.71</td>
<td>random</td>
<td>12.589</td>
</tr>
<tr>
<td>20 °C</td>
<td>0.324</td>
<td>0.199</td>
<td>99.99</td>
<td>random</td>
<td>12.223</td>
</tr>
<tr>
<td>30 °C</td>
<td>3.282</td>
<td>1.422</td>
<td>99.81</td>
<td>random</td>
<td>11.302</td>
</tr>
<tr>
<td>40 °C</td>
<td>6.270</td>
<td>2.032</td>
<td>99.99</td>
<td>random</td>
<td>9.974</td>
</tr>
<tr>
<td>50 °C</td>
<td>4.620</td>
<td>1.353</td>
<td>99.50</td>
<td>random</td>
<td>9.109</td>
</tr>
</tbody>
</table>
The C and K constants increased with the increase in temperature. The first is associated with the different chemical potentials between the monolayer and the upper layers; the second between the free water and the upper layers, and which, with rare exceptions, is close to but smaller than one (TIMMERMANN; CHIRIFE; IGLESIAS, 2001). Values greater than one are physically unsuitable, indicating infinite sorption.

The moisture sorption isotherms of the soursop powder are shown in Figure 1.

**Figure 1 - Water sorption isotherms of soursop powder**

An increase in the equilibrium moisture content with increasing water activity can be seen for a constant temperature. This behaviour manifests itself in the form of a sigmoid curve that reflects a Type III isotherm, a characteristic of foods that are rich in soluble compounds, such as coffee, apples and bananas, and that are high in sugars (BRUNAUER et al., 1940). The same behaviour was obtained by Moreira et al. (2013).

According to Cano-Higuita et al. (2015), in foods that are rich in such soluble sugars as glucose, fructose and sucrose, the increase in equilibrium moisture content is slow at low water activity values, this is followed by a sharp increase at intermediate and high water activity values. This behaviour is attributed to the predominant effect of the solvent-solute interaction associated with the dissolution of sugar (FABRA; CASTRO; CHIRALT, 2011).

The effect of temperature on the sorption isotherms of soursop powder can also be seen in Figure 1. At a constant value for water activity, there is a reduction in the equilibrium moisture content for an increase in temperature. This is due to an increase in the degree of molecular disorder of the water adsorbed on the surface of the product. As the temperature varies, excitement of the molecules, as well as the distance, and therefore, the attraction between them, also vary. Thus, for any given water activity, the amount of moisture sorption changes with the variation in temperature (MOHSENIN, 1986), a result of chemical and physical changes.

Analysing Table 3, which shows the parameters C₀, K₀, and the enthalpies associated with the GAB model, a positive value for the enthalpy of U₀ can be seen, indicating the occurrence of endothermic reactions. As explained by Oliveira et al. (2011), the reactions absorb energy from the environment in which the products are inserted. Furthermore, the authors state that a higher enthalpy value for this parameter can be expected, as the monolayer moisture content indicates the number of water molecules that are tightly bound to specific sites on the product surface, requiring larger amounts of energy to remove them.

**Table 3 - C₀, K₀, U₀ and the enthalpies associated with the GAB model**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Enthalpy (kJ kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₀</td>
<td>45.455 x 109</td>
<td>-2581.035</td>
</tr>
<tr>
<td>K₀</td>
<td>2.0238</td>
<td>-107.758</td>
</tr>
<tr>
<td>X_m₀ (% db)</td>
<td>0.8538</td>
<td>356.624</td>
</tr>
</tbody>
</table>

*Significant at 1% probability by t-test

Further analysing Table 3, negative enthalpy values are seen for the C₀ and K₀ parameters. These represent the difference in sorption heat between the monolayer and the multilayers, and the heat of vaporisation of the water and multilayers respectively (MUZAFFAR; KUMAR, 2016). The negative sign indicates the release of energy caused by the increased level of vibration of the water molecules due to the increase in working temperature (OLIVEIRA et al., 2017b).

From Figure 2, an increase can be seen in the integral isosteric heat of sorption for a decrease in the equilibrium moisture content, where the adjusted equation had a coefficient of determination of 99.34%. A similar trend is reported in the literature by authors such as Ascheri et al. (2009), for rhizome starch in *Hedychium coronarium* at a temperature range of 30 to 50 °C, and by Pedro, Telis-Romero and Telis (2010), for powdered passion fruit pulp at temperatures of 20, 30, 40 and 50 °C.

It is known that during the early stages of sorption (low moisture content) there are highly active polar sites with high interaction energy on the product surface that are covered with water molecules, forming a monomolecular layer. As the water molecules bind
chemically to these highly active sites, sorption takes place at less active sites (high moisture content), with less interaction energy and, consequently, a lower isosteric heat of sorption (PÉREZ-ALONSO et al., 2006).

The latent heat of vaporisation, which represents the minimum amount of energy required to evaporate the water molecules, was 2430.50 kJ kg$^{-1}$. It can be seen from Figure 2 that this was always greater than the latent heat of vaporisation of free water, up to an equilibrium moisture content of 50% db. This is because the energy binding the water molecules to the sorption sites is greater than the energy binding the water molecules to each other during the liquid phase (MASUZAWA; STERLING, 1968). From this point on, it reaches a minimum value of 2421.289 kJ kg$^{-1}$, indicating that the net isosteric heat becomes negative. This slightly negative value for a high equilibrium moisture content suggests the endothermic dissolution of the sugars in the adsorbed water.

The differential entropy (Figure 3), with an R$^2$ of 98.97%, showed the same trend as the integral isosteric heat of sorption, i.e. it decreased with increases in the equilibrium moisture content, indicating a loss of mobility of the water molecules in the product. According to Cano-Higuita et al. (2015), this represents the algebraic sum of molar differential entropy and total entropy of the water adsorbed on the solid at a particular hydration level, in addition to the change in order or disorder after new water molecules are adsorbed in the system at the same hydration level. For Goneli et al. (2013), the number of available adsorption sites that correspond to a specific energy level is proportional to the differential entropy, which describes the degree of disorder and the random movement of the water molecules.

Furthermore, negative entropy values are also seen from an equilibrium moisture content of 40% db, indicating a loss of mobility of the water molecules during sorption. The same was reported by Xiao and Tong (2013).

A change in Gibbs free energy during moisture sorption between the product and the environment can be defined as the energy required to transfer water molecules from the vapour state onto a solid surface, or from a solid surface into the vapour state. This amount can be considered a measure of the work done by the system during the adsorption or desorption process (KALEEMULLAH; KAILAPPAN, 2007). The values for Gibbs free energy decreased with increases in the equilibrium moisture content and temperature (Figure 4). The same was observed by Kaleemullah and Kailappan (2007), Oliveira et al. (2010) and Oliveira et al. (2011).

Furthermore, it can be seen that, irrespective of temperature, the Gibbs free energy tends to a constant value for increases in the equilibrium moisture content.

The regression equations for Gibbs free energy as a function of equilibrium moisture content (Xe) for each temperature, and their coefficients of determination, are shown in Table 4. This shows a good fit for the models.

The correlation between enthalpy and entropy for moisture sorption in soursop powder can be seen in Figure 5. The adjusted equation is shown in the graph, where the coefficient of determination, which describes the ability of the model to explain the observed values, was 99.99%.
Table 4 - Regression equations for Gibbs free energy as a function of equilibrium moisture content for each temperature, and their respective coefficients of determination

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Equation</th>
<th>R² (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>(\Delta G = 23.382** + 1137.061** \times \exp(-0.125** \times X_e))</td>
<td>99.57</td>
</tr>
<tr>
<td>20</td>
<td>(\Delta G = 29.781** + 1259.856** \times \exp(-0.131** \times X_e))</td>
<td>99.51</td>
</tr>
<tr>
<td>30</td>
<td>(\Delta G = 28.282** + 922.281** \times \exp(-0.119** \times X_e))</td>
<td>99.63</td>
</tr>
<tr>
<td>40</td>
<td>(\Delta G = 28.879** + 640.578** \times \exp(-0.109** \times X_e))</td>
<td>99.66</td>
</tr>
<tr>
<td>50</td>
<td>(\Delta G = 24.471** + 516.140** \times \exp(-0.104** \times X_e))</td>
<td>99.75</td>
</tr>
</tbody>
</table>

*Significant at 1% probability by t-test

Figure 4 - Gibbs free energy in soursop powder

Figure 5 - Correlation between enthalpy and entropy for moisture sorption in soursop powder, and the regression equation

The isokinetic and harmonic temperatures were 380.94 and 302.50 K respectively, confirming the suitability of the isokinetic theory; once \(T_B > T_{har}\), the process is controlled by enthalpy.

CONCLUSIONS

1. The GAB model effectively described the moisture sorption phenomenon in soursop powder;
2. The monolayer moisture content decreased with the increase in temperature of the sorption process, ranging from 12.589 to 9.109% db;
3. The enthalpy values related to the GAB model were negative, with a value of -2581.035 kJ kg\(^{-1}\) for \(C_0\) and -107.758 kJ kg\(^{-1}\) for \(K_0\);
4. The isosteric heat of sorption, entropy and Gibbs free energy showed a high correlation with the equilibrium moisture content, and the correlation between enthalpy and entropy was confirmed for moisture sorption in soursop powder.

REFERENCES


GAB model and the thermodynamic properties of moisture sorption in soursop fruit powder


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