

## Equilibrium Isotherms of a Biodegradable Polymer Polyhydroxybutyrate (PHB): Heat of Desorption Determination

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Polyhydroxybutyrate (PHB) belongs to a group of bacterial polyesters that may be considered as “green plastics”, because of their biodegradable nature. The knowledge of the relationship between moisture content and water activity is essential for drying and storage. The thermodynamic equilibrium is characterized by equilibrium isotherms, and its determination is essential for better understanding of mechanisms in drying operations. Results on desorption isotherms of PHB are not available in the literature. Thus, the aim of this study was to analyze the equilibrium isotherms of PHB using GAB (Guggenheim-Anderson-de Boer) and GDW (generalized D’Arcy and Watt) models, and to determine the heat of desorption using Clausius-Clapeyron equation. The moisture equilibrium data for desorption isotherms of PHB were investigated at 40, 50 and 60 °C using the gravimetric static method. The monolayer moisture contents (from 0.16 to 0.23 % d.b.) decreased with increasing temperature. The Clausius-Clapeyron equation was considered adequate to forecast the heat of desorption, which was estimated as a function of the moisture content.

### Introduction

Poly(hydroxyalkanoate)s (PHAs) constitute a class of biodegradable and biocompatible thermoplastic polyesters produced by a wide variety of microorganisms. Among the PHA family, many studies have focused on poly-3-hydroxybutyrate (PHB) (Sombatmankhong et al., 2007). The plastic-like properties of PHB makes it attractive to replace conventional non-degradable polymers such as polyethylene and polypropylene (Barud et al., 2010).

In Brazil, PHB is produced by bacterial fermentation of sugarcane in a process integrated to sugar and ethanol production. The process to obtain PHB granules consists of fermentation, crystallization, extraction, and drying (Mantelatto et al., 2008). After the extraction step, PHB has granular form, moisture content around 30% (w.b.) and particle mean size around 800 µm. Drying is a very important step in PHB production because an adequate post-processing is achieved only at moisture contents around 0.5 % (w.b) (Godoi et al., 2010).

It is well known that sorption isotherms are very important for design, modeling and optimization of many processes. The moisture sorption isotherm depicts the relation between equilibrium relative humidity and moisture content (Soysal and Oztekin, 1999). The knowledge of the temperature dependence of sorption phenomena provides valuable information about changes related to the thermodynamics of the system (Rizvi, 1995).

Results on desorption isotherms of PHB are not available in the literature. Hence, research on this field for a better and more comprehensive interpretation will be presented in this paper. The aims of this study were: (a) to determine the desorption isotherms of PHB at 40, 50 and 60 °C, (b) to evaluate the equilibrium isotherms of PHB using GAB (Guggenheim-Anderson-de Boer) and GDW (generalized D'Arcy and Watt) models, (c) to determine the heat of desorption using Clausius-Clapeyron equation.

## Materials and Methods

### Materials

Granules of PHB used in this work were provided by Biocycle® (Serrana - Brazil), before the drying step, having moisture content of 38.89 % (d.b.). The moisture content of PHB samples were determined by oven method at 105 °C during 24 h.

### Experimental procedure

Desorption isotherms were determined, in triplicate, by gravimetric static method using acid solutions. The isotherms were determined at temperatures of 40, 50 and 60 °C. The experiments to obtain the isotherms were carried out in glass jars, hermetically closed. Every jar was filled up to a quarter with various concentrations of sulfuric acid solutions (0.25 - 0.70 kg kg<sup>-1</sup>) to keep the water activity inside the bottles from 0.05 to 0.82, according to Perry and Green (1997). The samples were weighed and placed on a support in each jar, not allowing contact with the acid solution. The jars were kept in an incubator, under controlled temperature during the time necessary to reach constant weight. Measurements of the mass of each sample were taken at regular intervals in an electronic scale, with precision of 0.0001 g. The equilibrium condition was reached when the difference among consecutive measurements was ≤ 0.001 g, and at this condition, the moisture content analysis was carried out to determine the equilibrium moisture content.

### Mathematical description of the isotherms

Several mathematical models are available in the literature for description of the moisture sorption isotherms. GAB model (Guggenheim-Anderson-de Boer) is still one of the most popular models applied for description of water sorption in food science engineering (Furmaniak et al., 2009), particularly successful for water activities up to 0.9. The mathematical form of this model is:

$$M_e = \frac{r_m C K a_w}{(1-K a_w)(1-K a_w + C K a_w)} \quad (1)$$

where  $m_m$  is the monolayer capacity,  $C$  is the kinetic constant related to the sorption in the first layer,  $K$  is the kinetic constant related to multilayer sorption,  $a_w$  is the water activity.

The GDW (generalized D'Arcy and Watt) model was proposed initially for description of water sorption on carbons, and has been applied successfully in food engineering (Furmaniak et al., 2009). This model assumes the existence of the primary sorption centers where the mechanism sorption occurs, and that each primary adsorption site can create more than one secondary adsorption site (Furmaniak et al., 2007). Equation 2 represents GDW model.

$$M_g = \frac{m K a_w}{(1 + K a_w)} \cdot \frac{1 - k(1-w)a_w}{1 - k a_w} \quad (2)$$

where  $m$  is the maximum sorption value on primary centers,  $K$  and  $k$  are the kinetics constants connected with sorption on primary and secondary centers, and  $w$  is the parameter determining the ratio of molecules bonded to primary centers converted into secondary ones.

Non-linear regression analysis was done using the experimental data of equilibrium isotherms of PHB, using the software Statistica 7.0, resulting in estimation of the models parameters. Adequacy of the data fitting to the models was evaluated by the determination coefficient ( $R^2$ ).

For the determination of the net isosteric heat of desorption, an equation derived from Clausius–Clapeyron equation (Equation 3) was used and the isosteric heat of desorption was calculated by Equation 4.

$$\left( \frac{d(\ln a_w)}{d\left(\frac{1}{T}\right)} \right) = - \frac{q_{st}}{R} \quad (3)$$

$$Q_{st} = q_{st} + \Delta H_{vap} \quad (4)$$

where  $q_{st}$  is the net isosteric heat of sorption ( $\text{kJ mol}^{-1}$ ),  $R$  is the universal gas constant ( $\text{kJ mol}^{-1} \text{K}^{-1}$ ),  $T$  is the absolute temperature (K),  $a_w$  is the water activity,  $Q_{st}$  is the isosteric heat of desorption ( $\text{kJ mol}^{-1}$ ) and  $\Delta H_{vap}$  the heat of vaporization of water ( $\text{kJ mol}^{-1}$ ).

For the calculation of the isosteric heat, eight values of moisture contents from 0.05 to 0.60  $\text{kg kg}^{-1}$  (d.b.) were used. For each of these values,  $a_w$  was calculated using Equation (1) and the respective adjustment parameters. By plotting  $-\ln(a_w)$  versus  $1/T$ , for a specific moisture content, and then determining the slope ( $-q_{st}/R$ ), the net isosteric heat ( $q_{st}$ ) was obtained.

## Results and Discussion

Figure 1 illustrates the desorption isotherms at 40, 50 and 60 °C, for PHB. It can be verified that the curves presented sigmoidal shape, which is characteristic of most foods and biological materials, like polymer-organic compounds (Gocho et al., 2000). The sigmoidal nature of an isotherm has been described by numerous models and it is considered to consist of three parts. For low water activity (0-15 %), monolayer adsorption onto the internal surface is the dominant process; between 15 and 70 %

polylayer water formation in the micro capillaries occurs, and above 70 % the capillary condensation becomes increasingly dominant (Hill et al., 2009). The data also indicate that the equilibrium moisture content decreased with increasing temperature, at constant water activity.

Nonlinear regression analyses, using GAB and GDW models, were performed with the experimental desorption isotherm data. The results are shown in Table 1.

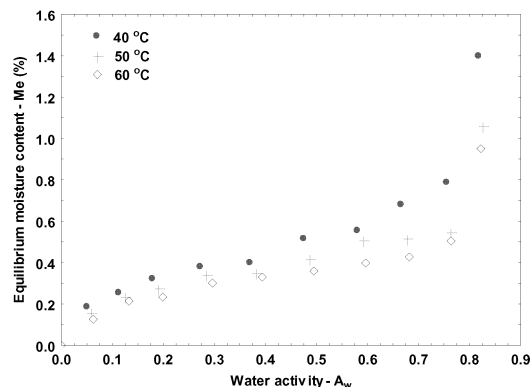


Figure 1: Desorption isotherms of PHB at different temperatures.

Table 1: Estimated parameters and  $R^2$ .

Constants	40 °C	50 °C	60 °C
<b>GAB</b>			
$m_m$ [%]	0.23	0.20	0.16
C	180.91	168.56	213.79
K	1.01	0.95	0.99
$R^2$ [%]	96.0	91.2	91.4
<b>GDW</b>			
m [%]	0.59	0.61	0.72
K	6.58	4.59	2.39
k	1.16	1.19	1.22
w	0.091	0.017	0.0009
$R^2$ [%]	99.5	99.3	98.9

Table 1 demonstrates that both models resulted in good fit to the experimental data. However, the GDW model provided higher determination coefficients ( $R^2 > 98\%$ ). The monolayer moisture content ( $m_m$ ) represents the moisture content of the material when the entire surface is covered with a unimolecular moisture layer (Ariahu et al., 2006). It was also observed that  $m_m$  decreased when temperature increased.

In GDW model the value of  $w$  is considerably smaller than unity, therefore, only a small amount of water molecules sorbed on primary sites converts into the secondary centers. Similar results were presented by Furmaniak et al. (2009) for semolina and milk powder.

Heat of desorption ( $Q_{st}$ ) as a function of the equilibrium moisture content is shown in Figure 2, for 60 °C. The isosteric heat of desorption varies with the amount of water adsorbed by the substrate. It is a way of measuring the energy required to break the

intermolecular forces between the molecules of water vapor and the adsorbent surface (Rizvi, 1995).

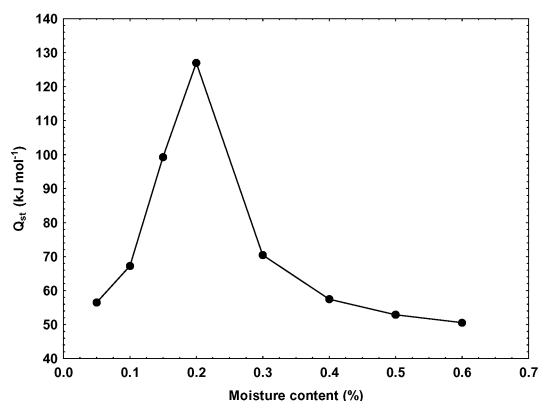


Figure 2: Heat of desorption for different moisture content of PHB.

The isosteric heat of desorption increased to a maximum (126 kJ mol<sup>-1</sup>) and then decreased with the increase of moisture content. The maximum isosteric heat of desorption was obtained at a moisture content of 20% (d.b.). Similar behavior was observed in other studies, as in the case of microalgae *Spirulina platensis* (Oliveira et al., 2009), mulberry (Maskan and Gogus, 1998), apple (Moraes et al., 2008) and cookies and corn snacks (Palou et al., 1997). The increase of the isosteric heat at low moisture contents can be explained considering the exposure of sorption sites of higher binding energy that was not previously available. After the maximum, the decrease of the isosteric heat with the amount of water sorbed can be qualitatively explained considering that initially, sorption occurs on most active available sites given rise to greater interaction energy. As these sites become occupied, sorption occurs in less active sites, resulting in lower heats of desorption (Palou et al., 1997).

## Conclusions

The desorption isotherms of PHB presented sigmoidal shape. Both models (GAB and GDW) resulted in good fit to the experimental data. The monolayer moisture content values for PHB, at different temperatures, were estimated by GAB model and ranged from 0.16 to 0.23 % (d.b.). The heat of desorption increased to a maximum (126 kJ mol<sup>-1</sup>) and then decreased with the increase in moisture content.

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