



Moisture sorption properties of chitosan

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ARTICLE INFO

Article history:

Received 6 April 2009

Received in revised form

27 August 2009

Accepted 3 September 2009

Keywords:

Differential entropy

Equilibrium isotherms

Heat of sorption

Pore size

ABSTRACT

The moisture equilibrium isotherms of chitosan were determined at 20, 30, 40, 50 and 60 °C, using the gravimetric static method. Experimental data were analyzed by the GAB, Oswin, Halsey and Smith equations. Isothermic heat and differential entropy of sorption were determined from the GAB model using the Clausius-Clapeyron and Gibbs-Helmholtz equations, and pore size distribution was calculated by the Kelvin and Halsey equations. The GAB and Oswin equations showed best fit to the experimental data with $R^2 \approx 99\%$ and low mean relative deviation values ($E\% < 10\%$). Monolayer moisture content values (from 0.12 to 0.20 kg kg⁻¹) and water surface area values (from 450 to 700 m² g⁻¹) decrease with increasing temperature. Isothermic heat and differential entropy of sorption were estimated as a function of moisture content. The Kelvin and Halsey equations were adequate for calculation of pore size distribution, which varied from 0.5 to 30 nm.

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1. Introduction

Chitosan is a biopolymer derived from chitin, a major component of crustacean shells such as crab, shrimp and crawfish. It has received considerable attention due to its commercial applications in the biomedical field, food and chemical industries (No, Park, Lee, & Meyers, 2002; Tan, Khor, Tan, & Wong, 1998). Chitin and chitosan are recommended as suitable functional materials, because these natural polymers have excellent properties such as biocompatibility, biodegradability, non-toxicity and adsorption properties (Ravi Kumar, 2000). Chitosan is obtained by chitin deacetylation, after this process, chitosan goes through purification process for obtainment of purified chitosan (Weska, Moura, Batista, Rizzi, & Pinto, 2007).

Isotherms provide significant information of process steps (such as drying and storage), thermodynamics and structure investigations. Numerous mathematical models for description of the moisture sorption behavior of foods are available in literature. Due to the complexity of foodstuffs, there is not one model that fits all cases well (García-Pérez, Cárcel, Clemente, & Mulet, 2008). Criteria used for selecting the most appropriate sorption model are the degree of fit to the experimental data and the simplicity of the model (Kaymak-Ertekin & Gedik, 2004). Knowledge on the isothermic heat of sorption is of great importance for designing equipment for dehydration processes and the qualitative understanding

of the state of water on the food surface (Tolaba, Peltzer, Enriquez, & Pollio, 2004). This is due to the fact that the vaporization heat of sorbed water may be higher than the vaporization heat of pure water, considering that food is dehydrated to low moisture levels (Rizvi, 1986). The differential entropy of sorption of a material is proportional to the number of available sorption sites at a specific energy level (Togrul & Arslan, 2006).

The evaluation of pore size distribution in porous materials is of great importance in drying practice (Strumillo & Kudra, 1986). Size of mesopores, defined by IUPAC (International Union of Pure & Applied Chemistry) as 2–50 nm, has long been studied through gas adsorption methods (Miyata, Endo, Ohmori, Akiya, & Nakaiwa, 2003). Historically, the Kelvin equation has been the most commonly employed model, however, the equation does not take into account the thickness of layers formed on the porous surface prior to condensation. A variety of methods attempt to account for film growth by coupling the Kelvin equation with a standard isotherm, or “t-curve”, in order to describe the thickness of the precondensation film on the pore walls (Lastoskie, Gubbins, & Quirke, 1993). The Halsey equation can be used to predict the thickness of the layer formed on the porous surface at a given water activity (Miyata et al., 2003).

The aims of this work were: (a) to determine the desorption isotherms of chitosan at 20, 30, 40, 50 and 60 °C, (b) to evaluate sorption models and compare their fit in describing the isotherms, (c) to determine thermodynamic functions such as the isothermic heat of sorption and the differential entropy and (d) to determine the pore size distribution of chitosan by the Kelvin and Halsey equations.

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2. Material and methods

2.1. Preparation of chitosan

Chitosan was produced by chitin deacetylation. Chitin was obtained from pink-shrimp (*Farfantepenaeus brasiliensis*) shell wastes, in an agitated tank, at room temperature, by the following steps (Piccin, Vieira, Gonçalves, Dotto, & Pinto, 2009): demineralization, which consists of reducing the ashes of the raw material, with hydrochloric acid solution 25 g L⁻¹ (2.5 L of acid solution for each kilogram of material mass), for two hours; deproteinization, where there is a reduction of the protein nitrogen of the shrimp wastes, with sodium hydroxide solution 50 g L⁻¹ (3 L of hydroxide solution for each kilogram of material mass), for two hours; and deodorization, for reducing shrimp's characteristic odor, with sodium hypochlorite solution 3.6 g L⁻¹ (5 L of hypochlorite solution for each kilogram of material mass), for three hours.

Deacetylation reaction was carried out in a reactor, under heating and stirring, by adding 2 L of sodium hydroxide solution (425 g L⁻¹) to 30 g of chitin. Reaction temperature was 130 °C and deacetylation was carried out for 90 min. Chitosan was purified according to the method given by Weska et al. (2007). Deacetylation degree was determined by the potentiometric titration method described by Broussignac, reported by Tolaimatea et al. (2000). Molecular weight of chitosan was determined by the intrinsic viscosity method described by Roberts and Domszy (1982). These experiments were carried out in triplicate, resulting in wet chitosan with moisture content of 0.94 kg kg⁻¹ (wet basis), deacetylation degree of 86 ± 2% and molecular weight of 170 ± 10 kDa.

2.2. Isotherm determination procedure

The gravimetric static method was used to determine the equilibrium moisture content of chitosan. The isotherms were determined at temperatures of 20, 30, 40, 50 and 60 °C.

The experiments to obtain the isotherms were carried out in eleven hermetically closed glass jars (height of 7 cm and diameter of 6 cm). Three gram of wet sample (moisture content approximately 0.94 kg kg⁻¹) was used in each jar and mass was measured every two days with a 0.001 g precision electronic scale (Kern model 430-21, Germany). Each jar was filled until a quarter full with various concentrations of sulfuric acid solutions (0.20–0.70 kg kg⁻¹) in order to keep a water activity of 0.043–0.890 inside the jars. The samples, placed on a support in each jar, were not in contact with the acidic solution. The jars stayed in an incubator with controlled temperature for the time necessary to reach constant weight. The equilibrium condition was attained within 13–15 days, when the difference among three consecutive weights were within 0.001 g; in this condition the moisture content analysis was carried out by drying in a conventional oven at 105 °C for 24 h, in order to determine the equilibrium moisture content. The concentration of sulfuric acid solutions were checked at the end of the experiments by titration with sodium hydroxide solution. Each experiment was carried out in triplicate. Values of water activity obtained through the different sulfuric acid solutions, at the different considered temperatures, were presented in Perry (1984).

2.3. Isotherms models and thermodynamics properties

The most commonly used isotherm models for moisture sorption isotherms of foods are the GAB model (Equation (1)), with a sound theoretical basis, and other semi-empirical and empirical models: Oswin (Equation (2)), Halsey (Equation (3)) and Smith (Equation (4)) (Barreiro, Fernández, & Sandoval, 2003; Kaya & Kahyaoglu, 2007).

The GAB model has been particularly successful for water activities up to 0.9 (Van den Berg, 1984).

$$M_e = \frac{M_m \cdot C \cdot k \cdot a_w}{(1 - k \cdot a_w) \cdot (1 - k \cdot a_w + C \cdot k \cdot a_w)} \quad (1)$$

$$M_e = A_1 \left(\frac{a_w}{1 - a_w} \right)^{B_1} \quad (2)$$

$$M_e = \left(\frac{-A_2}{\ln(a_w)} \right)^{1/B_2} \quad (3)$$

$$M_e = A_3 - B_3 \cdot \ln(1 - a_w) \quad (4)$$

where M_e is the equilibrium moisture content (kg kg⁻¹, dry basis), M_m is the monolayer moisture content (kg kg⁻¹, dry basis), a_w is the water activity and A_1 , A_2 , A_3 , B_1 , B_2 , B_3 , C , k are constants.

Monolayer moisture content was calculated using the GAB model. Once its value is known, the solid surface area can be determined by Equation (5) (Cassini, Marczak, & Noreña, 2006). The specific surface area plays an important role in determining the water binding properties of particulate materials.

$$S_0 = M_m \frac{1}{PM_{H_2O}} N_0 A_{H_2O} = 3.5 \cdot 10^3 M_m \quad (5)$$

where S_0 is the surface area (m² g⁻¹), M_m is the monolayer moisture content (kg kg⁻¹, dry basis), PM_{H_2O} is the molecular weight of water (18 g mol⁻¹), N_0 is Avogadro's number (6 × 10²³ molecules mol⁻¹) and A_{H_2O} is the area of one water molecule (1.06 × 10⁻¹⁹ m²).

The Clausius–Clapeyron equation is frequently used to predict the temperature effect on water activity, at a constant moisture content, and has the advantage of giving the adsorption or desorption heat for food materials depending on the isotherm data used (Ayrançi & Duman, 2005). Entropy change plays an important role in the energy analysis of food processing systems, and the differential entropy of sorption can be calculated by Gibbs–Helmholtz equation (Togrul & Arslan, 2006).

For the calculation of net isosteric heat (q_{st}) and differential entropy of sorption (S_d) seven values of moisture content from 0.05 to 0.50 kg kg⁻¹ (dry basis) were used. Through these values, the values of a_w were calculated using Equation (1) (GAB) and its adjustment parameters. By plotting $-\ln(a_w)$ versus $1/T$, for a specific moisture content of the material, and then determining the slope ($-q_{st}/R$) and intercept (S_d/R), the net isosteric heat (q_{st}) and differential entropy (S_d) of desorption were obtained (Kaya & Kahyaoglu, 2007).

$$-\ln a_w = \frac{q_{st}}{RT} - \frac{S_d}{R} \quad (6)$$

where q_{st} is the net isosteric heat of sorption (kJ mol⁻¹), S_d is the differential entropy (kJ mol⁻¹ K⁻¹), R the universal gas constant (kJ mol⁻¹ K⁻¹), T is the absolute temperature (K) and a_w is the water activity.

The Kelvin equation, Equation (7), is used for the calculation of critical radius. This equation applies primarily to the condensation region of the isotherm (Singh, Rao, Anjaneyulu, & Patil, 2001).

$$r_c = \frac{2\sigma V_M}{RT \ln(1/a_w)} \quad (7)$$

where r_c is the critical radius (m), σ is the surface tension (N m⁻¹), V_M is the molal volume of sorbate (m³ mol⁻¹), R is the universal gas constant (kJ mol⁻¹ K⁻¹), T is the temperature (K) and a_w is the water activity.

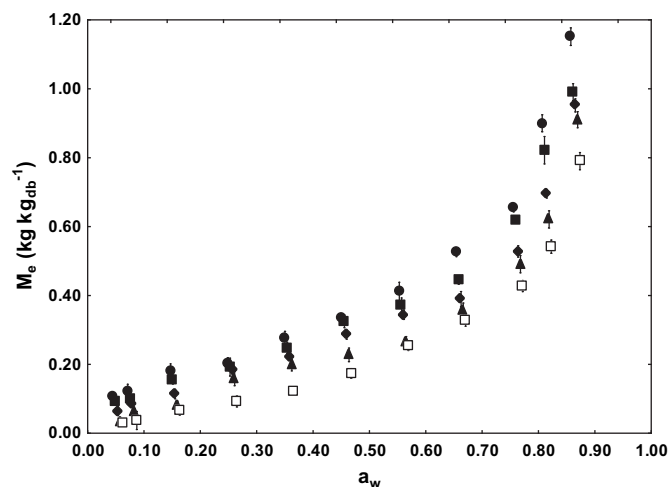


Fig. 1. Desorption equilibrium isotherms of chitosan at different temperatures: ● 20 °C, ■ 30 °C, ◆ 40 °C, ▲ 50 °C, □ 60 °C (mean values \pm standard error, in triplicate).

The thickness of the water adsorbed layer was calculated from the Halsey equation (Equation (8)) (Singh et al., 2001).

$$t = 0.354 \cdot \left(\frac{-5}{\ln a_w} \right)^{1/3} \quad (8)$$

where t is the multilayer thickness in nm.

Pore radius R_p may be obtained by the sum of the critical radius r_c , when the capillary condensation or evaporation occurs, and the multilayer thickness, t , shown in Equation (9) (Singh et al., 2001).

$$R_p = r_c + t \quad (9)$$

2.4. Statistical analysis

A nonlinear regression analysis by the least square method was carried out with the software Statistica 6.0 Windows (StatSoft Inc.,

USA) to evaluate the model parameters within the range of 0–0.9 water activity. The parameters were analyzed through the statistics- t of Student, which is the relation between the mean values of the parameters and its standard deviation value, and the level of significance was set at 0.05 in all cases. The validity of the statistical analysis was verified by the residues distribution (Box, Hunter, & Hunter, 1978). The coefficient of determination, R^2 , was one of the primary criteria used for selecting the best equation to define the sorption curves of chitosan. Fit quality was evaluated by calculating the mean relative percentage deviation modulus, $E\%$, according to Equation (10). The mean relative deviation is an absolute value that correlates the estimated and measured data. Low mean relative deviation values ($E\% < 10\%$) indicate good fit.

$$E\% = \frac{100}{N} \left(\sum_{i=1}^n \frac{|M_e^i - M_p^i|}{M_e^i} \right) \quad (10)$$

where N is the number of observations; M_e^i and M_p^i are the experimental and predicted values of the equilibrium moisture content, respectively.

3. Results and discussion

3.1. Isotherms equations

Moisture desorption isotherms (a_w versus M_e) of chitosan at the studied temperatures are shown in Fig. 1.

Analyzing Fig. 1, it can be verified that the isotherms curves of chitosan presented a sigmoidal shape, which is characteristic of a glassy polymer-organic on water vapor system (Gocho, Shimizu, Tanioka, Chou, & Nakajima, 2000; Kablan, Clément, Françoise, & Mathias, 2008).

A nonlinear regression analysis was carried out with the experimental desorption isotherm data, utilizing GAB, Oswin, Halsey and Smith models (Equations (1–4)). The results at different temperatures are shown in Table 1.

In Table 1, all models presented a good fit to the experimental data ($R^2 > 99\%$), except for the Smith model. The high values of R^2 at different temperatures showed that the good fit of the models is

Table 1
Adjustment parameters of isotherm models for chitosan.

Constants ^a	20 °C	30 °C	40 °C	50 °C	60 °C
GAB					
M_m (kg kg _{dwb} ⁻¹)	0.200 \pm 0.007	0.191 \pm 0.010	0.158 \pm 0.007	0.133 \pm 0.006	0.129 \pm 0.009
C	16.27 \pm 4.73	12.56 \pm 4.22	11.71 \pm 3.47	8.23 \pm 2.25	2.98 \pm 0.77
K	0.95 \pm 0.01	0.93 \pm 0.01	0.95 \pm 0.01	0.96 \pm 0.01	0.95 \pm 0.01
E (%)	5.84	6.58	7.37	9.52	7.98
R^2 (%)	99.65	99.54	99.62	99.69	99.73
Oswin					
A_1	0.369 \pm 0.007	0.338 \pm 0.006	0.287 \pm 0.005	0.232 \pm 0.005	0.181 \pm 0.003
B_1	0.572 \pm 0.012	0.561 \pm 0.012	0.575 \pm 0.013	0.640 \pm 0.013	0.704 \pm 0.009
E (%)	9.88	7.96	6.77	8.06	7.96
R^2 (%)	99.23	99.17	99.14	99.31	99.73
Halsey					
A_2	0.163 \pm 0.002	0.141 \pm 0.002	0.120 \pm 0.003	0.104 \pm 0.002	0.090 \pm 0.002
B_2	2.388 \pm 0.020	1.405 \pm 0.028	1.346 \pm 0.028	1.264 \pm 0.025	1.179 \pm 0.026
E (%)	5.74	8.45	13.58	20.98	24.09
R^2 (%)	99.57	99.16	99.07	99.19	99.04
Smith					
A_3	0.054 \pm 0.013	0.051 \pm 0.011	0.041 \pm 0.010	0.035 \pm 0.012	0.032 \pm 0.010
B_3	0.483 \pm 0.013	0.434 \pm 0.010	0.371 \pm 0.010	0.357 \pm 0.012	0.339 \pm 0.009
E (%)	11.44	9.27	6.86	14.16	23.07
R^2 (%)	97.93	98.27	97.72	96.87	97.78

^a Mean values \pm standard error (in triplicate).

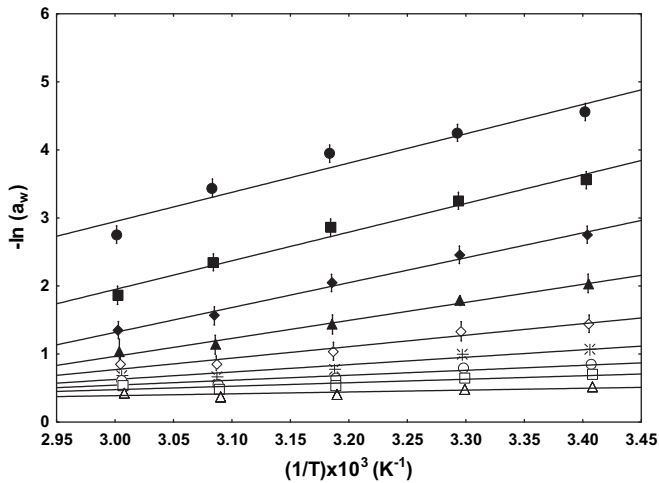


Fig. 2. Curves of $[-\ln(a_w)]$ versus $(1/T)$, at the analyzed temperatures: ● $M_e = 0.05 \text{ kg kg}^{-1}$, ■ $M_e = 0.10 \text{ kg kg}^{-1}$, ◆ $M_e = 0.15 \text{ kg kg}^{-1}$, ▲ $M_e = 0.20 \text{ kg kg}^{-1}$, ◇ $M_e = 0.25 \text{ kg kg}^{-1}$, * $M_e = 0.30 \text{ kg kg}^{-1}$, ○ $M_e = 0.35 \text{ kg kg}^{-1}$, □ $M_e = 0.40 \text{ kg kg}^{-1}$, △ $M_e = 0.50 \text{ kg kg}^{-1}$ (mean values \pm standard error, in triplicate).

independent of temperature. It can also be verified that the mean relative deviations ($E\%$) were lower than 10% for the GAB and Oswin models. A model's fit is satisfactory for practical purposes when $E\%$ is less than 10% (Kaymak-Ertekin & Gedik, 2004). It was verified that all parameters of the analyzed models presented high values of the statistics- t of Student, which is the relation between the mean value of the parameter and its standard deviation value. All parameters of the models were significant in the response values of the equilibrium moisture content (M_e) at the level of significance of 95% (the calculated value of each parameter by the nonlinear regression analysis presented P-level lower than 0.05). The residues presented random distribution in all regression analysis carried out (figures not shown).

The GAB model has a theoretical basis, while the other models are empirical or semi-empirical (Adebowale, Sanni, Awonorin, Daniel, & Kuye, 2007). According to Lomauro, Bakshi, and Labuza (1985) the GAB equation provide the best fit for more than 50% of the fruits, meats and vegetables analyzed. This model has been widely applied to describe equilibrium moisture isotherms in foodstuffs, and was recommended by the European Project COST90 (European Cooperation in Scientific and Technical Research) (García-Pérez et al., 2008). The prediction of monolayer moisture content values, M_m , shown in Table 1, is important since deterioration of food is very small below M_m . This is because water is strongly bound to the food below M_m and is not involved in any deteriorative reaction either as solvent or as one of the substrates. It can also be seen in Table 1 that M_m decreases with the increase of temperature. Kablan et al. (2008) determined moisture sorption isotherms of chitosan (deacetylation degree and molecular weight were 92% and 600 kDa, respectively) and chitin in granular powder, through adsorption isotherms at 4 °C. The GAB model was used to fit the experimental data providing values of monolayer moisture content of 0.076 and 0.047 ($\text{kg kg}_{\text{db}}^{-1}$) for chitosan and chitin, respectively.

3.2. Sorption properties

The specific surface area values of chitosan desorption were calculated by Equation (5) using the monolayer moisture values obtained from the GAB equation at the equilibrium temperatures of 20, 30, 40, 50 and 60 °C, resulting in 700, 670, 550, 465 and

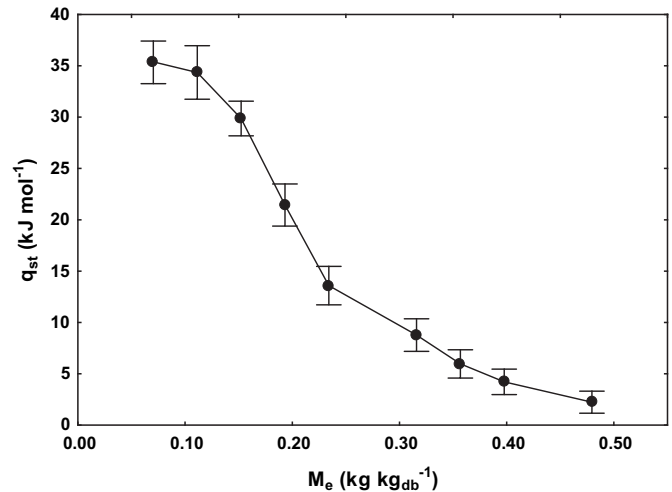


Fig. 3. Net isosteric heat of sorption for different moisture content of chitosan (mean values \pm standard error, in triplicate).

450 $\text{m}^2 \text{g}^{-1}$, respectively. These results indicate that the availability of specific surface areas for hydrophilic binding decrease with increasing temperature.

The calculated surface area values of chitosan were higher than the range commonly obtained for food products: 100–200 $\text{m}^2 \text{g}^{-1}$ (Labuza, 1968). Kablan et al. (2008) obtained surface area values of 267 $\text{m}^2 \text{g}^{-1}$ for adsorption of chitosan, at 4 °C, in granular powder form. Arslan and Togrul (2005) obtained values ranging from 373 to 380 $\text{m}^2 \text{g}^{-1}$ for desorption macaroni, at equilibrium temperatures from 25 to 45 °C. Tolaba et al. (2004) reported surface area values of quinoa grains from 200 to 350 $\text{m}^2 \text{g}^{-1}$ for desorption at different temperatures.

Aguerre, Suarez, and Viollaz (1989) indicated that the large sorption surface area of many biopolymers is due to the existence of an intrinsic microporous structure in the materials. The number and size of pores in the carbohydrate matrix determine the total sorption area and the pore surface influences the rate and extent of hydration (Sing, 2001).

Fig. 2 shows the isosteric curves. The linearity of the slopes seen in this figure shows that heat of sorption is independent of temperature at different values of equilibrium moisture content, except for higher equilibrium moisture content values ($M_e \geq 0.35 \text{ kg kg}^{-1}$, dry basis).

Fig. 3 shows that the net isosteric heat of sorption decreases with the equilibrium moisture content. This decrease can be qualitatively explained by considering that sorption initially occurs at the most active sites, giving rise to the greatest interaction energy. As the moisture content increases, the sites available for water sorption decrease, resulting in lower values of q_{st} (Tsami, Maroulis, Marinou-Kouris, & Saravacos, 1990). The total heat of sorption is useful for estimating the energy requirement for water removal during the drying operation. The total heat of sorption at 60 °C (chitosan industrial drying temperature) is obtained by the sum of the net isosteric heat (Fig. 3) and the vaporization heat of pure water (assumed at 42.5 kJ mol^{-1}).

The differential entropy of sorption versus moisture content is shown in Fig. 4. Initially chitosan's differential entropy decreases with increasing moisture content, but after a moisture content of 0.10 kg kg^{-1} , it increases rapidly with increasing moisture content. The same behavior was observed for various materials, as presented by Togrul and Arslan (2006) for stored rice, Togrul and Arslan (2007) for walnut kernels, Kaya and Kahyaoglu (2007) for safflower petals and tarragon and Ariaahu, Kaze, and Achem (2006)

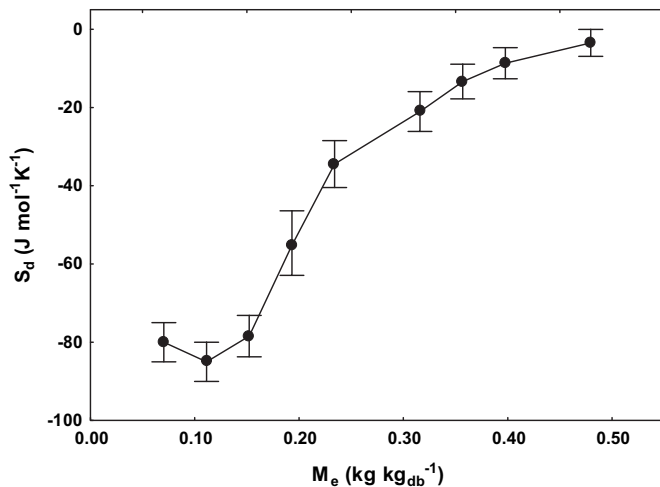


Fig. 4. Differential entropy for different moisture content of chitosan (mean values \pm standard error, in triplicate).

for tropical freshwater crayfish. At low water activity range, a decrease in differential entropy values is possibly caused by the strongest binding sites with water molecules and the solid as suggested by McMinn and Magee (2003).

In Fig. 4, for all the moisture content range, entropy values were negative. Rizvi (1986) attributed this to the fact that the products contain more polar groups, which bind water more strongly, while Iglesias, Chirife, and Viollaz (1976) attributed negative entropy values to the existence of chemical adsorption and/or structural modifications of the adsorbent.

The critical radius (r_c), multilayer thickness (t) and average pore size (R_p) were calculated according to Equations (7–9) respectively, at 60 °C (temperature of chitosan drying). The volume values of the liquid (V) in relation to 1 kg of dry material contained in the pores with radius R_p was calculated with the moisture content and the adsorbed water density. The radius, moisture content and pores volume values are presented in Table 2. The average pore size (R_p) of chitosan at all studied moisture contents was found in range from 0.5 to 30 nm, which can be classified as micropores and mesopores according to the IUPAC classification.

Table 2
Radius, moisture content and pore volume values at different water activity, at 60 °C.

a_w	R_p (m) $\times 10^9$	M^a (kg kg _{db} ⁻¹)	V^a (m ³ kg ⁻¹) $\times 10^5$
0.05	0.51	0.018 \pm 0.005	1.80 \pm 0.54
0.10	0.66	0.034 \pm 0.009	3.46 \pm 0.95
0.15	0.80	0.050 \pm 0.013	5.06 \pm 1.28
0.20	0.95	0.065 \pm 0.015	6.64 \pm 1.54
0.25	1.10	0.081 \pm 0.017	8.25 \pm 1.78
0.30	1.27	0.097 \pm 0.019	9.91 \pm 1.98
0.35	1.45	0.115 \pm 0.021	11.68 \pm 2.18
0.40	1.66	0.134 \pm 0.023	13.60 \pm 2.38
0.45	1.91	0.155 \pm 0.025	15.73 \pm 2.68
0.50	2.20	0.178 \pm 0.028	18.14 \pm 2.85
0.55	2.55	0.206 \pm 0.030	20.93 \pm 3.14
0.60	2.99	0.238 \pm 0.034	24.25 \pm 3.45
0.65	3.54	0.278 \pm 0.038	28.30 \pm 3.88
0.70	4.28	0.328 \pm 0.044	33.42 \pm 4.48
0.75	5.30	0.395 \pm 0.052	40.13 \pm 5.30
0.80	6.84	0.486 \pm 0.065	49.41 \pm 6.58
0.85	9.39	0.621 \pm 0.086	63.19 \pm 8.72
0.90	14.5	0.845 \pm 0.127	85.96 \pm 12.8
0.95	29.7	1.289 \pm 0.229	129.95 \pm 9.98

^a Mean values \pm standard error (in triplicate).

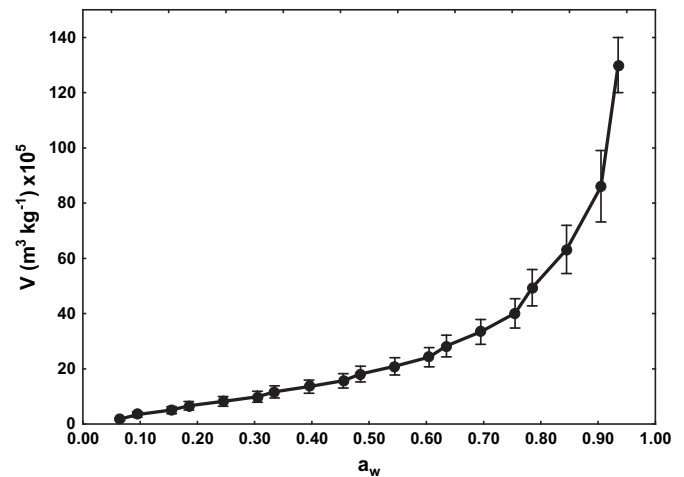


Fig. 5. Pore volume versus water activity, at 60 °C (mean values \pm standard error, in triplicate).

Fig. 5 shows the pores volume (V) versus the water activity (a_w). An increase in the desorbed water content is shown in water activity (a_w) values around 0.40, due to the increase in the amount of desorbed water by capillary evaporation or condensation within the pore in multilayer. According to Sing (2001), the capillary condensation is generally responsible for the filling of mesopores and macropores ($R_p \geq 2$ nm); however, capillary condensation is a secondary process, since it is always preceded by multilayer desorption/adsorption on the pore walls. Thus, in Fig. 5 the outset of capillary condensation is indicated by an upward deviation from the corresponding multilayer isotherm (Type II), and is attained at higher a_w (≥ 0.80). Also, this indicates that the amount of desorbed water increases rapidly, and accurate pore size distribution is obtained only in the chitosan mesopores. Therefore, it is important to calculate the pore radius (R_p) in order to accurately evaluate multilayer thickness (t) and critical radius (r_c) of capillary evaporation or condensation, especially when the a_w is lower than 0.40.

4. Conclusions

The desorption isotherms of chitosan presented a sigmoidal shape, which is characteristic of glassy polymer-organic isotherms on water vapor systems. All models presented a good fit to the experimental data ($R^2 > 99\%$), except the Smith model for equilibrium isotherms of chitosan. The best fits were the GAB and Oswin models, with a relative percentage deviation ($E\%$) lower than 10%. The monolayer moisture content values for chitosan, at different temperatures, were estimated by GAB model and ranged from 0.12 to 0.20 kg kg⁻¹, on a dry basis. The obtained surface area values varied from 451.5 to 700 m² g⁻¹.

The net isosteric heat of sorption for chitosan was independent of temperature except for higher equilibrium moisture content values (≥ 0.35 kg kg⁻¹). The differential entropy of chitosan decreased with increasing moisture content, and after a moisture content of 0.10 kg kg⁻¹ it rapidly increased. The pore size distribution of chitosan, calculated by the Kelvin equation and multilayer thickness (Halsey equation), presented values in the range of 0.5–30 nm.

Acknowledgements

The authors thank CNPq (National Council of Scientific and Technological Development), Brazil, for the financial support conceded in the execution of this study.

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Nomenclature

- a_w : water activity, dimensionless
 A_{H_2O} : area of one water molecule, m^2
 A_1 : constant in Equation (2), dimensionless
 A_2 : constant in Equation (3), dimensionless
 A_3 : constant in Equation (4), dimensionless
 B_1 : constant in Equation (2), dimensionless
 B_2 : constant in Equation (3), dimensionless
 B_3 : constant in Equation (4), dimensionless
 C : constant in Equation (1), dimensionless
 ΔH_{vap} : vaporization heat of pure water, $kJ\ mol^{-1}$
 $E\%$: mean relative deviation, %
 k : constant in Equation (1), dimensionless
 M : moisture content of the sample (d.b.), $kg\ kg^{-1}$
 M_e : equilibrium moisture content of the sample (d.b.), $kg\ kg^{-1}$
 M_{ei} : experimental values of equilibrium moisture (d.b.), $kg\ kg^{-1}$
 M_{pi} : predicted values of equilibrium moisture (d.b.), $kg\ kg^{-1}$
 M_m : monolayer moisture content of the sample (d.b.), $kg\ kg^{-1}$
 N : number of experimental points, dimensionless
 N_0 : Avogadro's number, molecules mol^{-1}
 PM_{H_2O} : molecular weight of water, $g\ mol^{-1}$
 q_{st} : net isosteric heat of desorption, $kJ\ mol^{-1}$
 r_c : critical radius, m
 R : universal gas constant, $kJ\ mol^{-1}\ K^{-1}$
 R_p : pore radius, m
 S_0 : surface area, m^2
 S_d : differential entropy, $kJ\ mol^{-1}\ K^{-1}$
 t : multilayer thickness, m
 T : temperature, K
 V : pore volume with relation to 1 kg of dry material, $m^3\ kg^{-1}$
 V_M : molal volume of sorbate, $m^3\ mol^{-1}$
 ρ : density, $kg\ m^{-3}$
 σ : surface tension, $N\ m^{-1}$