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# Water adsorption isotherms of carboxymethyl cellulose, guar, locust bean, tragacanth and xanthan gums

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ABSTRACT

Water adsorption isotherms of carboxymethyl cellulose (CMC), guar gum (GG), locust bean gum (LBG), tragacanth gum (TG) and xanthan gum (XG) were determined at different temperatures (20, 35, 50, and 65 °C) using a gravimetric method. Several saturated salt solutions were selected to obtain different water activities in the range from 0.09 to 0.91. Water adsorption isotherms of tested hydrocolloids were classified like type II isotherms. In all cases, equilibrium moisture content decreased with increasing temperature at each water activity value. Three-parameter Guggenheim–Anderson–de Boer (GAB) model was employed to fit the experimental data in the water activity range and statistical analysis indicated that this model gave satisfactory results. CMC and GG were the most and the least hygroscopic gums, respectively. Sorption heats decreased with increasing moisture content. Monolayer moisture content evaluated with GAB model was consistent with equilibrium conditions of maximum stability calculated from thermodynamic analysis of net integral entropy. Values of equilibrium relative humidity at 20 °C are proposed to storage adequately the tested gums.

## 1. Introduction

The use of different additives as thickeners, stabilizers, emulsifiers and gelling agents increases in many industrial processes to achieve determined properties of final products (Rosell, Collar, & Haros, 2007). Particularly, food industry mainly demands gums like solid powders or splits that are added during processing to different liquid or solid systems. The hygroscopic nature of hydrocolloids is an important factor on moisture, texture and quality of food materials (Brown, 2007). The knowledge of the water equilibrium conditions between gums and atmosphere is fundamental for the selection of adequate process conditions due to physicochemical properties, microbial safety and other characteristics depend on water activity (Rizvi, 1986). Specifically, water sorption characteristics are essential in relation to stability and acceptability of food products, selection of drying and storage conditions and packaging materials (Bahloul, Boudhrioua, & Kechaou, 2008). Food systems typically exhibit type II and III water sorption isotherms according to the BET classification (Brunauer, Deming, Deming, & Teller, 1940). These isotherms can be obtained for water adsorption or desorption processes by increasing or decreasing water activity of material. These processes are not fully reversible (Bell & Labuza, 2000).

Experimental water sorption isotherms are based on the determination (commonly at atmospheric pressure) of equilibrium moisture content and water activity at constant temperature. In the literature there are a large number of available empirical and semi-empirical equations to establish mathematical relationships among these variables and are usually performed by means of experimental data fitting (Bell & Labuza, 2000). These models can be also employed for evaluating some thermodynamic properties, which provide an understanding of adsorbed water properties and associated energy requirements (Fasina, 2006). In fact, BET (Brunauer, Emmett, & Teller, 1938) and GAB models (Van den Berg & Bruin, 1981) are often selected to fit complete experimental sorption isotherms and the involved parameters have physical meaning. Particularly, both models are typically used to determine interfacial area and pore sizes of biopolymer systems by means of the evaluation of the monolayer moisture content. Nevertheless, it seems more adequate, for these purposes, to employ other models (such as Langmuir model) with more appropriate theoretical basis (i.e. absence of solid–gas interface) because give more consistent results with those reported by other experimental techniques (Kocherbitov, Ulvenlund, Briggner, Kober, & Arnebrant, 2010; Kocherbitov, Ulvenlund, Kober, Jarring, & Arnebrant, 2008). Other relevant application of sorption isotherm modelling is to estimate the optimal conditions of product storage or packaging

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through the BET or GAB monolayer moisture content (Bell & Labuza, 2000). GAB model is usually selected because can fit adequately the equilibrium sorption data at low and high water activities. It would be interesting to establish relationships between the monolayer moisture content determined by GAB model and thermodynamic properties like net integral entropy to corroborate the minimization of deleterious physicochemical changes.

Selected gums (carboxymethyl cellulose (CMC), guar gum (GG), locust bean gum (LBG), tragacanth gum (TG) and xanthan gum (XG)) are natural polysaccharides employed in many industrial processes. By its properties, it has been extensively used in many applications as emulsifier, thickener, texturizer, stabilizer, mouthfeel and body agent (Verbeken, Dierckx, & Dewettinck, 2003). Namely, CMC is a linear polymer of β-D-glucose that derivates from cellulose where some of the hydroxyl groups are substituted with carboxymethyl groups. The properties of CMC depend on the degree of substitution (from 0.4 to 1.5) and the length of the cellulose chain (Imeson, 2010). Galactomannans (GG and LBG) are polysaccharides consisting of a mannose backbone with galactose side groups. The main chain consists of (1–4) linked β-D-mannose residues and the side chain of (1–6) linked α-D-galactose. These gums show different approximate mannose:galactose ratios, 2:1 and 4:1, respectively (Williams, 2007). TG is a slightly acidic salt consisting of two fractions. The acidic bassorin (insoluble fraction) has a chain of (1–4) linked α-D-galacturonic acid units some of which are substituted at O-3 with β-D-xylopyranosyl units and some of these being terminated with galactose or fucose. Tragacanthin (water soluble) is a branched arabinogalactan (Imeson, 2010). XG is an extracellular polysaccharide produced by the bacterium *Xanthomonas campestris*. It is a polysaccharide with a β-D-glucose backbone like cellulose, but every second glucose unit is attached to a trisaccharide consisting of mannose, glucuronic acid, and mannose. The mannose closest to the backbone has an acetic acid ester on carbon 6, and the mannose at the end of the trisaccharide is linked through carbons 6 and 4 to the second carbon of pyruvic acid (Williams, 2007).

Recently, some studies are available for sorption properties of guar gum (Vishwakarma, Shivhare, & Nanda, 2011), xanthan gum (Basu, Shivhare, & Mujumdar, 2007), pectin (Panchev, Slavov, Nikolova, & Kovacheva, 2010) or konjac glucomannan (desorption characteristics) (Yan et al., 2012). However, scarce detailed information is available in the literature on water sorption behaviour of selected hydrocolloids. Therefore, the main aim of this work is to obtain the experimental water adsorption isotherms of several hydrocolloids (CMC, GG, LBG, TG and XG) over a wide range of temperatures and water activities of interest. The specific objectives include experimental data correlation using GAB model, the statistical analysis of the goodness of fitting, the evaluation of some thermodynamic properties and the proposal of the optimal conditions for gums preservation.

## 2. Materials and methods

### 2.1. Preparation of samples

The studied hydrocolloids were CMC sodium salt (Panreac, Barcelona, Spain), GG (Sigma–Aldrich, St. Louis, MO), LBG (Alimentaria Adín, Valencia, Spain), TG (Merck, Darmstadt, Germany) and XG (Sigma–Aldrich, St. Louis, MO). Dry basis of the gums was obtained using a vacuum oven at 70 °C and 15 kPa (AOAC, 1995).

In order to assure the water adsorption process takes place at all water activities and temperatures tested samples were air dried (temperature: 40 °C and relative humidity: 0.05) using a climatic chamber (Challenge 250, Angelatoni Industries, Perugia, Italy). Drying operation finished when water activity of samples, measured by Novasina device (Thermoconstanter TH200, Pfaffikon, Switzerland), was lower than 0.08.

### 2.2. Experimental data for water sorption isotherms

The equilibrium moisture content, $X$ (kg water/kg d.b.), at several temperatures (20, 35, 50, and 65 °C) and over a wide water activity, $a_w$ (–), range (from 0.09 up to 0.91) of CMC, GG, LBG, TG and XG were experimentally determined following gravimetric static procedure based on the device proposed by Evans and Critchfield (1933). The different relative humidities of the atmospheres were created using several saturated salt (KOH, LiCl, $MgCl_2$, $K_2CO_3$, $Mg(NO_3)_2$, $NH_4NO_3$, NaCl, KCl and $BaCl_2$) solutions prepared following previous recommendations (Greenspan, 1977). Triplicate samples (approximately, 0.5 g) were stored on Petri dishes inside jars in a constant relative humidity atmosphere and were periodically weighed until to reach constant weight (±0.0005 g) in an analytical balance (SI-234 Denver Instrument, accuracy ± 0.0001 g). At water activity (>0.6), small amounts of crystalline thymol were placed in the jars in order to avoid microbial spoilage of samples. Eight weeks were necessary to achieve the equilibrium. The moisture content referred to dry basis of each sample was determined by standard method (AOAC, 1995). Water activity of samples was randomly measured to corroborate that the equilibrium was reached using the Novasina apparatus.

### 2.3. Experimental data modelling

The experimental data were fitted to Guggenheim, Anderson and de Boer (GAB) model (Anderson, 1946; de Boer, 1968; Van den Berg & Bruin, 1981) and it is described by the following equation:

$$X = \frac{X_M C K a_w}{[(1 - K a_w)(1 - K a_w + C K a_w)]} \quad (1)$$

The parameters $X_M$, $C$ and $K$ were estimated by non-linear regression procedure employing Table Curve software (Jandel Scientific). These parameters depend on temperature, $T$ (K), according to Arrhenius equations (Kim & Bhowmik, 1994):

$$X_M = X_{M0} \exp\left(\frac{H}{RT}\right) \quad (2)$$

$$C = C_0 \exp\left[\frac{h_M - h_N}{RT}\right] \quad (3)$$

$$K = K_0 \exp\left[\frac{h_L - h_N}{RT}\right] \quad (4)$$

where $X_M$ ((kg (kg d.b.)$^{-1}$)) is the monolayer moisture content, $C$ (–) is related to water sorption heat of the first layer (monolayer) and $K$ (–) involves the water sorption heat of multilayer. $X_{M0}$ ((kg (kg d.b.)$^{-1}$)), $C_0$ (–) and $K_0$ (–) are the pre-exponential fitting parameters. $R$ (8.314 J (mol K)$^{-1}$) is the ideal gas constant. The average heat of condensation of water vapour, $h_L$ (kJ mol$^{-1}$), is calculated in the range of temperature from 20 to 65 °C by Eq. (5):

$$h_L = 45.04 - 0.0438(T - 273) \quad (5)$$

where $H$ (kJ mol$^{-1}$) represents the heat of GAB model, $h_M - h_N$ (kJ mol$^{-1}$) shows the difference between monolayer and multilayer sorption enthalpy and $h_L - h_N$ (kJ mol$^{-1}$) represents the difference between the heat of condensation and multilayer sorption enthalpy (Van den Berg & Bruin, 1981).

### 2.4. Analysis of thermodynamic properties

The net isosteric sorption heat or net differential enthalpy, $q_{st}$ (kJ mol$^{-1}$), is defined by the difference between total isosteric sorption heat, $Q_{st}$ (kJ mol$^{-1}$), and condensation heat. Estimation of $q_{st}$ at constant moisture content can be performed using the Clausius–Clapeyron equation (Soekarto & Steinberg, 1981):

$$\ln\left(\frac{a_{w2}}{a_{w1}}\right)\bigg|_X = \frac{-q_{st}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{6}$$

The net equilibrium heat of sorption or net integral enthalpy, $q_{eq}$ (kJ mol$^{-1}$), represents the total energy available for to do work. It is calculated in a similar manner to the differential enthalpy, but at constant spreading pressure instead of constant moisture content. The variation in net integral enthalpy with moisture content indicates the water–substrate interactions in relation to the interactions between water molecules (Fasina, Ajibola, & Tyler, 1999; Rizvi, 1986).

Differential entropy, $S_d$ (J (mol K)$^{-1}$) of water adsorbed is proportional to the number of available sorption sites corresponding to a specific energy level. It can be calculated from Gibbs–Helmholtz equation as follows:

$$S_d = \frac{-q_{st} - \Delta G}{T} \tag{7}$$

where $\Delta G$ (J mol$^{-1}$) is the free Gibbs energy of water. Substituting the free Gibbs energy by its definition equation ($\Delta G = RT \ln a_w$), a new equation that relates $q_{st}$, $S_d$ and $a_w$ is obtained:

$$\ln a_w\big|_X = \frac{-q_{st}}{RT} - \frac{S_d}{R} \tag{8}$$

At constant moisture content, $S_d$ and $q_{st}$ can be obtained by linear fitting.

The evaluation of integral properties must be performed at constant spreading pressure. The spreading pressure, $\Pi$ (J m$^{-2}$), is the force applied in the plane of the surface that must be exerted perpendicular to each unit length of edge to keep the surface from spreading. It represents the surface excess energy and is considered as the increase in surface tension of bare sorption sites due to sorbed molecules (Fasina et al., 1999). This parameter can be estimated using an analytical procedure that involves the relationship between moisture content and water activity (Smith, Van Ness, & Abbott, 2001).

$$\Pi = \frac{K_B T}{A_m} \int_0^{a_w} \frac{\theta}{a_w}\, d(a_w) \tag{9}$$

where $K_B$ ($1.38 \times 10^{-23}$ J K$^{-1}$) is the Boltzmann's constant, $T$ is the absolute temperature (K), $A_m$ ($1.06 \times 10^{-19}$ m$^2$) represents the area of a water molecule and $\theta = X/X_M$. Spreading pressure can be obtained using GAB model, Eq. (1), resulting after the substitution and integration:

$$\Pi = \frac{-K_B T}{A_m} \ln\left[\frac{1 - K a_w}{1 - K(1 - C) a_w}\right]_0^{a_w} \tag{10}$$

Net integral entropy, $q_{eq}$ (J mol), describes the degree of disorder, randomness of motion and other statistical approach related to water sorption by food product. This parameter is a measure of mobility of adsorbed water molecules. The net integral enthalpy is calculated in a manner to the net differential enthalpy, Eq. (6), but at constant spreading pressure. Net integral entropy, $S_{eq}$ (J (mol K)$^{-1}$) is defined by the difference between the integral entropy of water adsorbed in the foodstuff and the entropy of pure liquid water in equilibrium with vapour. This entropy is usually employed in terms of order–disorder of water adsorbed molecules. Minimum value of $S_{eq}$ is related to the highest stability of the product (Bonilla, Azuara, Beristain, & Vernon-Carter, 2010). For a thermodynamic system, this entropy is given by (Aviara, Ajibola, & Oni, 2004):

$$S_{eq} = \frac{-q_{eq}}{T} - R \ln a_w|_\Pi \tag{11}$$

where $a_w|_\Pi$ is obtained at constant spreading pressure at different temperatures.

### 2.5. Statistical analysis

The values of GAB model parameters corresponding to water adsorption isotherms of tested hydrocolloids at each temperature were submitted to one-factor analysis of variance (ANOVA). Critical $F$ values ($\alpha = 0.05$) were used to evaluate if the factor is significant. In the case of positive significance, post hoc analyses using the Duncan comparison test ($\alpha = 0.05$) were performed to establish statistical differences between the calculated means of the parameters at each temperature (SPSS 18.0 statistical package).

The goodness of fitting of GAB model was evaluated by means of the coefficient of determination ($R^2$), the root mean squared error (RMSE), and the mean relative deviation (MRD). These parameters are calculated by using the following expressions:

$$\mathrm{RMSE} = \left[\frac{1}{N}\sum_{i=1}^{N}(X_{exp} - X_{cal})^2\right]^{1/2} \tag{12}$$

$$\mathrm{MRD} = \frac{1}{N}\sum_{i=1}^{N}\frac{|X_{exp} - X_{cal}|}{X_{exp}} \tag{13}$$

where $N$ is the number of samples and $X_{exp}$ and $X_{cal}$ (kg water/kg d.b.) represent the experimental and calculated equilibrium moisture content, respectively.

RMSE and the MRD are both measures of the deviation between experimental data. Low values for the RMSE and MRD indicate a high ability of the model to describe the experimental behaviour. These statistical parameters may be combined into the following performance index:

$$\Phi = \frac{R^2}{(\mathrm{RMSE})(\mathrm{MRD})} \tag{14}$$

Thus, higher $\Phi$ values indicate a better adequacy of the model to describe the experimental behaviour.

Furthermore, a series of statistical indices ($\gamma$, $\chi^2$ and $z_r$) were employed in order to corroborate the adequate selection of GAB model for assayed isotherms. These statistical indices were previously proposed (Ruiz-López & Herman-Lara, 2009) to determine whether a given model should be used to fit the experimental data. These authors also proposed the rejection criteria, which measure the statistical significance and precision of the parameter and the assessment of the regression assumptions, whereas a lumped index quantifies the fitness quality of the model. The model discrimination procedure can be summarized as follows: reject any model where $\gamma < 1$, $\chi^2 > 5.99$ and $z_r > 1.96$. More detailed information was previously reported in the paper aforementioned.

## 3. Results and discussion

### 3.1. Experimental water adsorption isotherms

Experimental data of equilibrium moisture content vs. water activity of tested hydrocolloids for adsorption process at different temperatures are shown in Fig. 1 ((a) CMC, (b) GG, (c) LBG, (d) TG and (e) XG). At each temperature, equilibrium moisture content increased with increasing water activity in all tested hydrocolloids following the shape corresponding to type II isotherms according Brunauer's classification (Brunauer et al., 1940). The equilibrium moisture content decreased with increasing temperature at each water activity. This effect can be explained because at high temperatures, the activation of the water molecules changes to higher energy levels and the links become less stable and break away from the water-binding sites of hydrocolloid, consequently the equilibrium moisture content decreases (Palipane & Driscoll, 1992). Particularly, experimental data of xanthan gum are according to

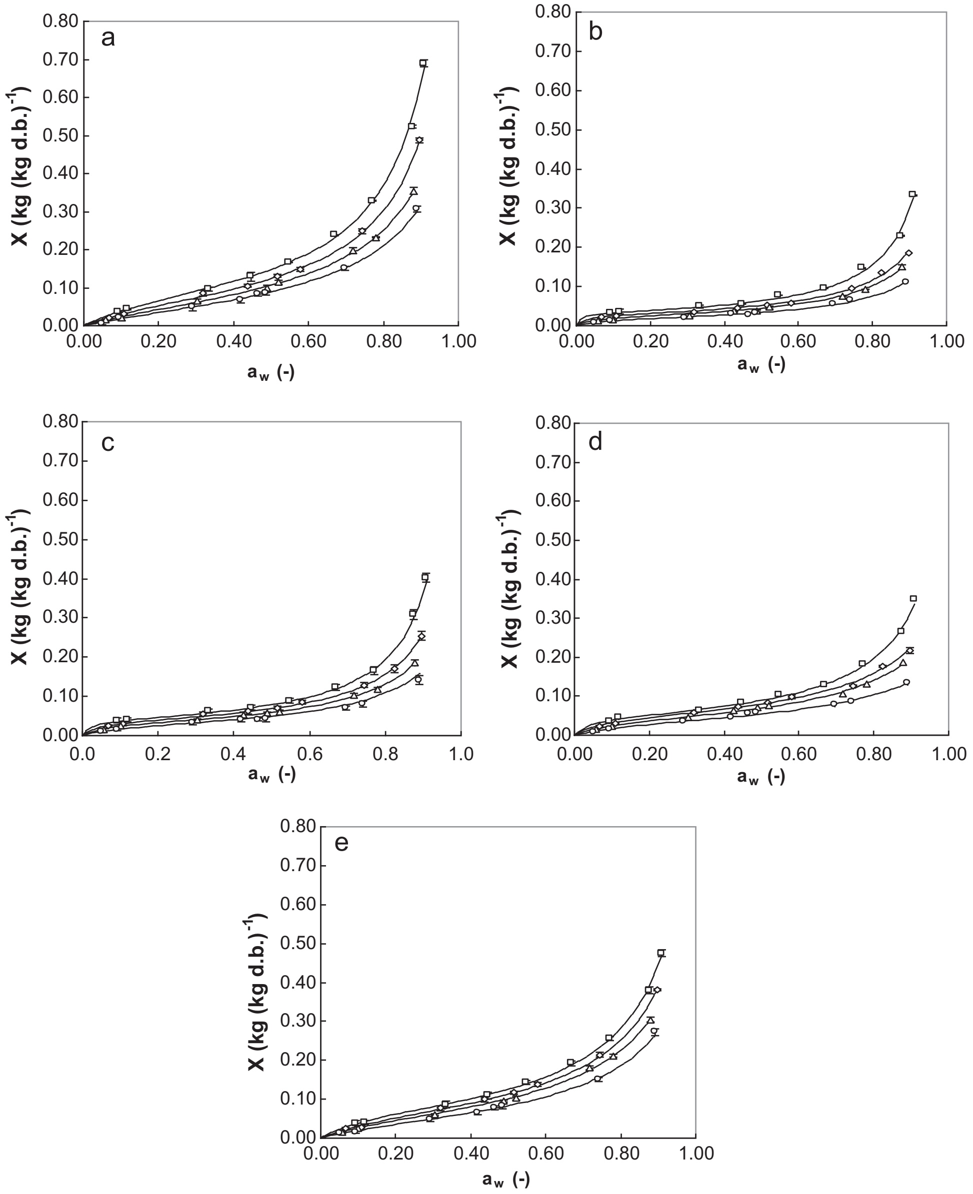

**Fig. 1.** Water adsorption isotherms of (a) carboxymethyl cellulose, (b) guar, (c) locust bean, (d) tragacanth and (e) xanthan gums at different temperatures: (□) 20, (◊) 35, (Δ) 50 and (○) 65 °C. Lines (—) correspond to GAB model (Eqs. (1)–(4)).

those previously found in the range of temperature from 30 to 70 °C by Basu et al. (2007). On the other hand, tested guar gum showed hygroscopic characteristics in the same range that guar gum splits and higher than guar gum grain determined between 10 and 40 °C (Vishwakarma et al., 2011).

### *3.2. Modelling of experimental data*

For all tested gums, experimental data were successfully fitted by GAB model (Eq. (1)). The adequate selection of this model was established taking into account the satisfactory values obtained for different statistical parameters (Ruiz-López & Herman-Lara, 2009) such as $R^2$ (>0.983), RMSE (<0.015), MRD (<0.088), $\Phi$ (>2228), $\gamma$ (>$7.34 \times 10^3$), $\chi^2$ (<4.49), $z_r$ (<0.997) (Table 1). In this Table are summarized the statistical parameters of the nonlinear regression analysis for GAB model data.

Table 2 collects the GAB parameters ($X_M$, $C$ and $K$) values for all studied hydrocolloids. The analysis of $X_M$ is useful at low water activities to evaluate the hygroscopic characteristics of the surface of each gum. At high water activity values other phenomena (phase transitions, capillarity, etc.) may take place that depend simultaneously on physicochemical properties and porous structure of the material. Particularly, $X_M$ showed the following order CMC > XG > TG > LBG > GG at constant temperature. These values are related to chemical structure and composition of each gum. GG and LBG are polymers formed by mannose and galactose monomers without acid or ionic groups in the structure and water molecules are linked by hydrogen bonds with accessible hydroxyl groups. TG is composed by an acidic fraction that contains galacturonic acid units which increase hygroscopic characteristics of gum and other fraction composed by arabinogalactan polymer. The frequency of glucuronic and pyruvic acids and acetic acid esters in XG is relevant and their high polarity explains the high $X_M$ values. Finally, the degree of substitution of hydroxyl groups by carboxymethyl groups explain by its ionic character that CMC shows the highest values of $X_M$ of the tested gums. It is also remarkable that in all cases GAB parameters values decreased significantly with increasing temperature. Values of the parameters ($C_0$, $K_0$, $X_{M0}$, $(h_M - h_N)$, $(h_L - h_N)$

**Table 1**
Statistical parameters for goodness evaluation of non-linear fitting with GAB model for experimental data of assayed gums.

| Hydrocolloids | Statistical parameters | | | | | | |
|---|---|---|---|---|---|---|---|
| | $R^2$ | RMSE | MRD | $\Phi$ | $\gamma$ | $\chi^2$ | $z_r$ |
| Carboxymethyl cellulose | 0.983 | 0.015 | 0.088 | 2228 | $7.34 \times 10^{3}$ | 3.43 | 0.977 |
| Guar gum | 0.995 | 0.005 | 0.059 | 4407 | $5.51 \times 10^{12}$ | 3.11 | 0.428 |
| Locust bean gum | 0.998 | 0.004 | 0.031 | 9551 | $1.75 \times 10^{10}$ | 0.974 | 0.249 |
| Tragacanth gum | 0.996 | 0.005 | 0.044 | 5141 | $5.71 \times 10^{7}$ | 0.789 | 0.703 |
| Xanthan gum | 0.996 | 0.008 | 0.047 | 3591 | $3.01 \times 10^{5}$ | 4.49 | 0.612 |

**Table 2**
Values of GAB model (Eq. (1)) parameters for water adsorption isotherms of tested hydrocolloids at several temperatures.[A]

| Parameters | Temperature (°C) | | | |
|---|---|---|---|---|
| | 20 | 35 | 50 | 65 |
| Carboxymethyl cellulose | | | | |
| $X_M$ | $0.091 \pm 0.001^{a}$ | $0.081 \pm 0.001^{b}$ | $0.077 \pm 0.001^{c}$ | $0.069 \pm 0.001^{d}$ |
| $C$ | $5.9 \pm 0.1^{a}$ | $4.8 \pm 0.1^{b}$ | $3.7 \pm 0.1^{c}$ | $3.2 \pm 0.1^{d}$ |
| $K$ | $0.957 \pm 0.006^{a}$ | $0.937 \pm 0.002^{b}$ | $0.903 \pm 0.004^{c}$ | $0.885 \pm 0.002^{d}$ |
| Guar gum | | | | |
| $X_M$ | $0.032 \pm 0.001^{a}$ | $0.028 \pm 0.001^{b}$ | $0.025 \pm 0.001^{c}$ | $0.020 \pm 0.001^{d}$ |
| $C$ | $99.9 \pm 0.9^{a}$ | $40.6 \pm 0.6^{b}$ | $20.0 \pm 0.2^{c}$ | $12.1 \pm 0.3^{d}$ |
| $K$ | $0.992 \pm 0.004^{a}$ | $0.951 \pm 0.002^{b}$ | $0.948 \pm 0.002^{c}$ | $0.927 \pm 0.005^{d}$ |
| Locust bean gum | | | | |
| $X_M$ | $0.041 \pm 0.001^{a}$ | $0.038 \pm 0.001^{b}$ | $0.034 \pm 0.001^{c}$ | $0.030 \pm 0.001^{d}$ |
| $C$ | $41.0 \pm 0.6^{a}$ | $23.8 \pm 0.4^{b}$ | $15.7 \pm 0.2^{c}$ | $9.8 \pm 0.2^{d}$ |
| $K$ | $0.987 \pm 0.005^{a}$ | $0.954 \pm 0.004^{b}$ | $0.934 \pm 0.002^{c}$ | $0.914 \pm 0.003^{d}$ |
| Tragacanth gum | | | | |
| $X_M$ | $0.050 \pm 0.001^{a}$ | $0.049 \pm 0.001^{a}$ | $0.045 \pm 0.001^{b}$ | $0.038 \pm 0.001^{c}$ |
| $C$ | $21.7 \pm 0.4^{a}$ | $14.2 \pm 0.3^{b}$ | $9.6 \pm 0.3^{c}$ | $7.6 \pm 0.2^{d}$ |
| $K$ | $0.939 \pm 0.005^{a}$ | $0.875 \pm 0.002^{b}$ | $0.869 \pm 0.002^{c}$ | $0.817 \pm 0.002^{d}$ |
| Xanthan gum | | | | |
| $X_M$ | $0.077 \pm 0.001^{a}$ | $0.074 \pm 0.001^{a}$ | $0.070 \pm 0.001^{b}$ | $0.061 \pm 0.001^{c}$ |
| $C$ | $8.2 \pm 0.2^{a}$ | $5.9 \pm 0.1^{b}$ | $5.2 \pm 0.1^{c}$ | $4.3 \pm 0.1^{d}$ |
| $K$ | $0.924 \pm 0.004^{a}$ | $0.908 \pm 0.002^{b}$ | $0.892 \pm 0.005^{c}$ | $0.879 \pm 0.003^{d}$ |

[A] Data are presented as means ± standard deviation. Data value with different superscript letters in row are significantly different, $p \leq 0.05$.

and $H$) of Arrhenius relationships (Eqs. (2)–(4)) corresponding to $C$, $K$ and $X_M$ are shown in Table 3. These values are within range that those found for other hydrocolloids like guar gum (Vishwakarma et al., 2011). The estimated $(h_M - h_N)$ values are positive, due to the strong exothermic interaction of water vapour with primary sorption sites of the material (Moreira, Chenlo, Torres, & Vallejo, 2008). The $(h_L - h_N)$ values are smaller and positives which is in agreement with the literature (Al-Muhtaseb, McMinn, & Magee, 2004). Water adsorption isotherms using GAB model including temperature effect are plotted by lines in Fig. 1.

### 3.3. Thermodynamic properties analysis

The relationship between net isosteric sorption heat, $q_{st}$, and moisture content for studied gums at the average temperature of the studied temperature range (20–65 °C) is shown in Fig. 2. In all cases, sorption heats decreased with increasing equilibrium moisture content. The highest values of $q_{st}$ were approximately 37.0, 27.0, 24.0, 12.8, 11.7 kJ mol$^{-1}$ for GG, LBG, TG, CMC and XG, respectively. These values are in a good agreement with the $(h_M - h_N)$ values estimated by GAB model, Table 3. Less hygroscopic hydrocolloids showed the highest sorption heats below $X_M$. These values of energy indicate that at low moisture content water is strongly bound to polar sites of the material (Bonilla et al., 2010; McMinn & Magee, 2003). These trends for sorption heats were similar to other hydrocolloids previously reported in the literature (Vishwakarma et al., 2011).

On the other hand, the variation of spreading pressure, Eq. (10), with water activity for CMC and GG at 20 and 65 °C as example of studied hydrocolloids are shown in Fig. 3. The results indicate that the spreading pressure increases with water activity, and decreases with temperature, at a given water activity. These spreading pressure trends with temperature and water activity were also found in starch gels (McMinn, Al-Muhtaseb, & Magee, 2004). Spreading pressure has been used as the driving force responsible for diffusion in porous solid (Skaar & Babiak, 1982). High values of spreading pressure indicate high affinity of water molecules to active sites. Obviously, CMC shows spreading pressures higher than GG because CMC is more hygroscopic (higher equilibrium moisture content at the same water activity) than GG.

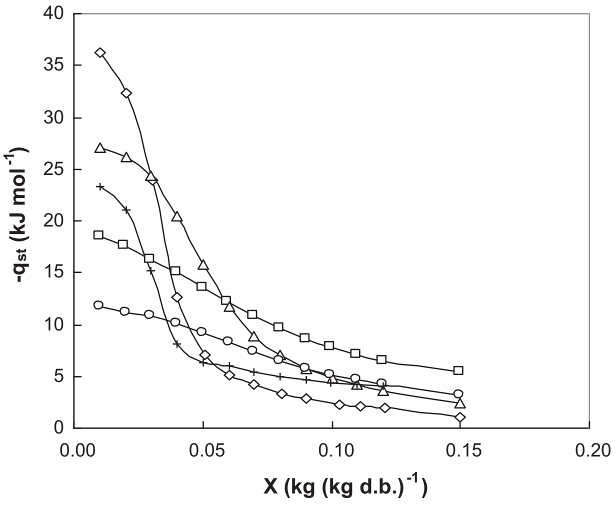

**Fig. 2.** Net isosteric heats of sorption vs. equilibrium moisture content: carboxymethyl cellulose (□), guar gum (◊), locust bean gum (+), tragacanth gum (△) and xanthan gum (○) at average temperature of studied temperature range (20–65 °C).

**Table 3**
Values of parameters of Eqs. (2)–(4) for tested gums.

| Parameters | $C_0$ (–) | $K_0$ (–) | $X_{M0}$ (kg (kg d.b.)$^{-1}$) | $H$ (kJ mol$^{-1}$) | ($h_M - h_N$) (kJ mol$^{-1}$) | ($h_L - h_N$) (kJ mol$^{-1}$) |
|---|---|---|---|---|---|---|
| Carboxymethyl cellulose | $5.0 \times 10^{-2}$ | 0.52 | $1.2 \times 10^{-2}$ | 4.8 | 11.6 | 1.5 |
| Guar gum | $1.0 \times 10^{-5}$ | 0.62 | $1.0 \times 10^{-3}$ | 8.5 | 38.7 | 1.1 |
| Locust bean gum | $1.0 \times 10^{-3}$ | 0.56 | $4.2 \times 10^{-3}$ | 5.6 | 25.9 | 1.4 |
| Tragacanth gum | $7.0 \times 10^{-3}$ | 0.36 | $7.2 \times 10^{-3}$ | 4.8 | 19.5 | 2.3 |
| Xanthan gum | $7.2 \times 10^{-2}$ | 0.63 | $1.4 \times 10^{-2}$ | 4.1 | 11.5 | 0.9 |

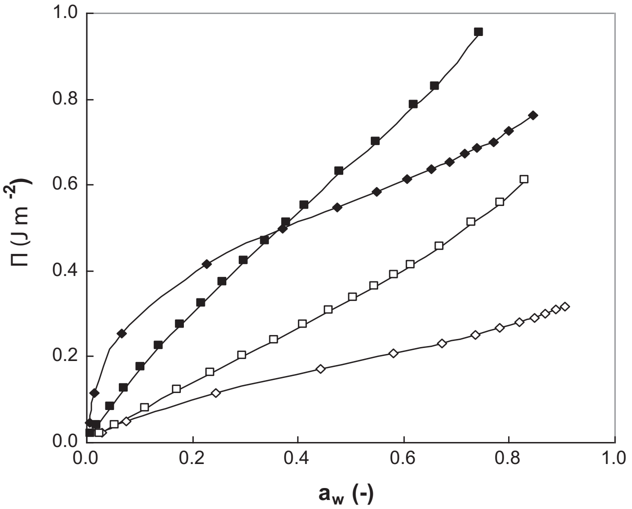

**Fig. 3.** Spreading pressure vs. water activity: carboxymethyl cellulose (■, □) and guar gum (♦, ◊) at 20 and 65 °C, respectively.

The behaviour of differential and net integral entropies, Eqs. (7) and (11), with moisture content at different temperatures 20 and 65 °C, is shown in Fig. 4(a) for CMC as example of tested gums. It can be observed that both entropy curves show maximum values of ($-S_d$) and ($-S_{eq}$) with stronger dependence of differential entropy with moisture content. The shape of the curves is the same independently on temperature, but the maximum values decrease with increasing temperature. The net integral entropy, $S_{eq}$, values decreased at low moisture content and reached characteristic minimum values for each hydrocolloid, Fig. 4b. Similar trends have been reported for other food products (Bonilla et al., 2010; Fasina et al., 1999; Kaya & Kahyaoglu, 2007). These minimum net integral entropy values are possibly caused by the water fixation (loss of rotational freedom and randomness) due to the strongest binding sites with water molecules and solid (McMinn & Magee, 2003). Additional adsorbed water above the critical moisture content increased the net integral entropy by the apparition of water multilayers along with swelling phenomena of the solid matrix. This critical moisture content can be considered the point of maximum stability of the product because water is strongly fixed and is less available to participate in spoilage reactions (Bonilla et al., 2010). Really, it would be more correct to determine the interval of moisture content where the net integral entropy remains practically constant because minimum is not very pronounced, Fig. 4. In fact, considering only an increase of the minimum value of entropy of 5%, the optimal moisture content (kg (kg d.b.)$^{-1}$), (and corresponding water activity) intervals at 20 °C were 0.027–0.090 (0.06–0.29) for CMC, 0.018–0.030 (0.02–0.06) for GG, 0.020–0.037 (0.02–0.09) for LBG, 0.023–0.049 (0.04–0.18) for TG and 0.031–0.078 (0.08–0.30) for XG. It is noteworthy that the monolayer moisture content values, $X_M$ (kg (kg d.b.)$^{-1}$), obtained directly from GAB model, Table 2, correspond practically to the highest value of the interval given by the minimum net integral entropy. This result was also found at each tested temperature. From these results, $X_M$ can be interpreted like the maximum adsorbed water content to maintain stable a product or, in the case of desorption process, the minimum target moisture content that a product has to be dried to achieve its stabilization.

## 4. Conclusions

Water adsorption isotherms determined experimentally for carboxymethyl cellulose, guar, locust bean, tragacanth and xanthan gums in the temperature range (20–65 °C) are type II. The equilibrium moisture content of studied hydrocolloids increases with increasing water activity at each temperature and decreases with increasing temperature at constant water activity. GAB model fits adequately the adsorption isotherms of tested hydrocolloids over the assayed range of temperatures and water activities. GAB parameters were satisfactorily correlated with temperature to evaluate some heats of sorption and particularly, monolayer moisture content values were related to chemical composition and structure of biopolymers. The presence of acid and ionic units in the chemical structure explains in acceptable agreement the found hygroscopic

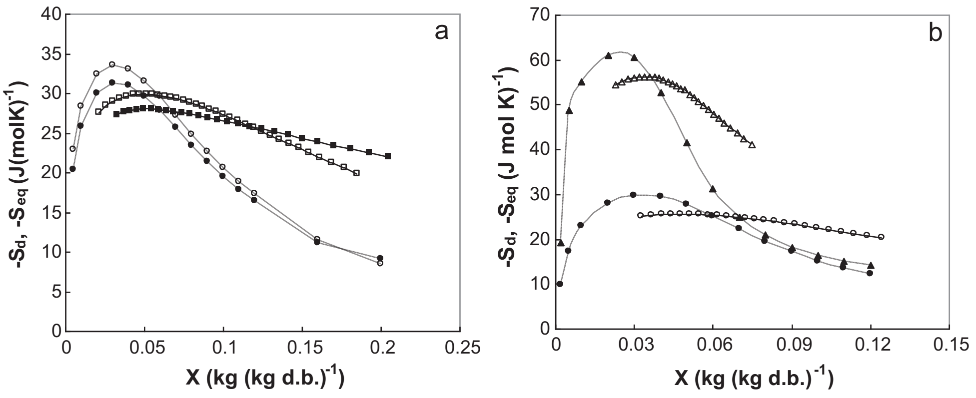

**Fig. 4.** Differential and net integral entropy vs. equilibrium moisture content (a) carboxymethyl cellulose at 20 (◊, □), and 65 °C (♦, ■) and (b) tragacanth gum (▲, △) and xanthan gum (●, ○) at 20 °C, respectively.

sequence of tested gums: GG < LBG < TG < XG < CMC. High values of spreading pressure indicate high affinity of water molecules to active and the same sequence was observed. Monolayer moisture content obtained from GAB model corresponded to the highest values of the optimal range for product preservation obtained from net integral entropy analysis. Atmospheres with low relative humidity (6–29% for CMC, 2–6% for GG, 2–9% for LBG, 4–18% for TG and 8–30% for XG) are proposed as the most suitable for tested gums storage at 20 °C.

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