
MOISTURE SORPTION PROPERTIES AND STORAGE STABILITY CONDITIONS OF A NUTRACEUTICAL SYSTEM MICROENCAPSULATED BY SPRAY DRYING

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MOISTURE SORPTION PROPERTIES AND STORAGE STABILITY CONDITIONS
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PROPIEDADES DE ADSORCIÓN DE HUMEDAD Y CONDICIONES DE
ESTABILIDAD EN ALMACENAMIENTO DE UN SISTEMA NUTRACÉUTICO
MICROENCAPSULADO POR SECADO POR ASPERSIÓN

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Abstract
The adsorption isotherms of a nutraceutical system microencapsulated by spray drying were determined at 20, 35 and 40
°C. Experimental data of the isotherms were fitted using the GAB and Caurie models and the integral thermodynamic
functions (enthalpy and entropy) were estimated by the Clausius-Clapeyron equation. The Kelvin and Halsey equations
were adequate for calculation of pore radius which varied from 0.67 to 8.15 nm. The point of maximum stability (minimum
integral entropy) was found between 3.61 and 3.81 kg H₂O/100 kg d.s. (corresponding to water activity, a_w, of 0.19-0.37).
Enthalpy-entropy compensation for the microcapsules showed two isokinetic temperatures. The first isokinetic temperature
was observed at low moisture contents (< 3.81 kg H₂O/100 kg d.s.) and was controlled by changes in the entropy of water,
whereas the second isokinetic temperature was considered to be enthalpy-driven (3.81-20 kg H₂O/100 kg d.s.).

Keywords: sorption isotherms, pore radius, minimum integral entropy, enthalpy-entropy compensation, water activity.

Resumen
Se determinaron las isoterms de adsorción de un sistema nutracéutico microencapsulado por secador por aspersión, a
20, 35 y 40°C. Los datos experimentales de las isoterms se ajustaron a los modelos de GAB y Caurie y las funciones
termodinámicas integrales (entalpía y entropía) se estimaron con la ecuación de Clausius-Clapeyron. Las ecuaciones de
Kelvin y Halsey se adecuaron para el cálculo del radio de poro, el cual se encontró de entre 0.67- 8.15 nm. El punto de
máxima estabilidad (mínimo de entropía integral) se encontró entre 3.61 y 3.81 kg H₂O/100 kg s.s. (correspondiente a la
actividad de agua, a_W, de 0.19-0.37). La compensación entalpía-entropía, presentó dos temperaturas isocinéticas. La
primera temperatura isocinética, se encontró a bajo contenido de humedad (< 3.81 kg H₂O/100 kg s.s.) y fue controlada
por cambios en la entropía del agua, mientras que la segunda temperatura isocinética fue controlada por la entalpía (3.81-20
kg H₂O/100 kg s.s.).

Palabras clave: isoterms de adsorción, radio de poro, mínimo de entropía integral, compensación entalpía-entropía,
actividad de agua.
1 Introduction

In food systems, water is one of the most important components where it could exist as free water or bound water (immobilized water). The latter is not available for microbial growth or chemical reactions, generally responsible of spoilage; therefore it is relevant to generate information on various aspects of bound water in food systems. The main and essential way in which the immobilization of the water is measured is through the consideration of water activity and its relationship to moisture content (Lewicki, 2004; Singh et al., 2006).

The depression of water activity observed in foods has been attributed to a combination of factors, each of which may be predominant in a certain range of moisture content within a food. These factors include solute-water interactions, capillary forces and water associated with specific sites. Several explanations have been made as: the nature of active sites, monomolecular adsorption on polar sites and multimolecular adsorption on specific sites (Rizvi, 1986). Different isotherm models based on this explanations have arisen in order to describe the relation between moisture content and water activity, such as GAB model (Guadarrama-Lezama et al., 2014) (multimolecular adsorption), Caurie model (Caurie, 2005) (monomolecular adsorption) and the Dubinin-Radushkevich model (Sonwane and Bhatia, 2006) (for micropore filling). Moisture sorption isotherm of food describes the equilibrium relationship between the water activity and food moisture content at constant temperature, giving an insight into the moisture-binding characteristic of a food (Ramírez-Miranda et al., 2014). Sorption isotherms can be used to investigate structural features of the food matrix, such as specific surface area, pore radius and volume, and crystallinity. Such data can be used for selecting appropriate storage conditions and packaging systems that lead to optimize or maximize the retention of aroma, colour, texture, nutrients and biological stability (Pérez-Alonso et al., 2006; Velázquez-Gutiérrez et al., 2015; Cano-Higuita et al., 2015).

In porous materials the rate and extent of hydration of the food materials is, greatly, decided by the surface properties of pores. Furthermore, the temperature at each pore is likely to affect the rate of entry and exit of water molecules. The knowledge of number and size of the pores in solid matrix is important as they are closely related to control the mass transfer making that the surface area, pore volume, and the pore radius very important parameters. Among these techniques, those based on effective capillary size, as the Kelvin equation, are the most common for measurements of pore size (Mitropoulos, 2008).

The thermodynamic functions establish optimum storage and stability conditions. For example, a change in free energy can indicate the affinity of the adsorbent for water, and provide a spontaneous or non-spontaneous criterion. Changes in enthalpy can be associated with bonding of repulsion forces between water and the food matrix. Furthermore, entropy changes may define the degree of order or disorder existing in the adsorbent-adsorbate system (Apostolopoulos and Gilbert, 1990; Viveros-Contreras et al., 2013). The kinetic compensation effect has been widely observed in various areas such as physics, chemistry, biology and thermal analysis. Fontan et al. (1982) suggested the existence of a linear relationship between enthalpy and entropy for water sorption in some foods. Moreover, the hydrophobic and hydrophilic interactions between water and other molecules can be explained from entropic and enthalpic mechanisms and the pore-water interaction (Azuara and Beristain, 2006).

Based on the above, the aims of this work were: (a) to interpret the mechanism of the sorption process of a nutraceutical system microencapsulated by spray drying; (b) to determine the pore radius of microcapsules by the Kelvin and Halsey equations (c) to study the sorption thermodynamic functions of a nutraceutical system microencapsulated by spray drying; (d) to obtain information about the enthalpic and entropic mechanisms during sorption process; (e) to establish the most suitable storage conditions for microcapsules where the minimum integral entropy occurs.

2 Materials and methods

2.1 Materials

Muitle leaves were purchased from a local greenhouse (Toluca, State of Mexico, Mexico), and the Muitle aqueous extract (MAE) was obtained according to the method proposed by Pavón-García et al. (2011). Chia seeds (Salvia hispanica L.) were provided by farmers of Atlixco, State of Puebla, Mexico. Chia oil (CO) extraction was performed according to the method proposed by Rodea-González et al. (2012). Ascorbic acid (AA) with 99.8% purity was purchased from Sigma-Aldrich Química S.A. de C.V. (Toluca,
State of Mexico, Mexico). Panodan SDK (esters of monoglycerides and diglycerides of diacetyl tartrate acid), a water-soluble surfactant (WS), and Grindsted PGPR 90 (esters of polyglycerol and polyricinoleate fatty acids) an oil-soluble surfactant (OS), were both purchased from Dannova Química S.A. de C.V. (Mexico City, Mexico). Mesquite gum (MG) hand collected in the form of tear drops from Prosopis laevigata trees in the Mexican State of San Luis Potosí and purified as indicated by Vernon-Carter et al. (1996); Gum Arabic (Acacia senegal) (GA) purchased from Industria Ragar, S.A. de C.V. (Mexico City, Mexico); and Maltodextrin DE10 (MD, Maltadex™) purchased from Complementos Alimenticios S.A. de C.V. (Naucalpan, State of Mexico, Mexico) were used as protective colloids. Bidistilled water was used in all the experiments, and sodium azide (Hycel biotech, MA, USA). Goodness of fit was evaluated using the relative percentage difference between the experimental and predicted values of moisture content, or mean relative 

2.2 Formulation and preparation of double \( W_1/O/W_2 \) emulsion

A water-in-oil-in-water double emulsion (\( W_1/O/W_2 \)) was prepared at room temperature (25 ± 1°C) using a two-stage emulsification procedure. In the first stage, a \( W_1/O \) emulsion was formulated with a 0.5 dispersed phase mass fraction. Total emulsifier concentration in \( W_1/O \) was 8% (w/w) with OS/WS ratio of 4:1 (Carrillo-Navas et al., 2012; Dzul-Cauich et al., 2013). The inner aqueous phase was a 1% w/w aqueous solution of AA in MAE, and this mixture was added drop-wise to the oil phase (\( O = CO+WS+OS \)) using an Ultra-Turrax T50 Basic homogenizer (IKA® WERKE Works Inc., Wilmington, NC, USA) at 5200 rpm for 5 min. In the second stage, the dispersed phase mass fraction was settled at 0.25 and the requisite amount of \( W_1/O \) primary emulsion was re-emulsified (7600 rpm for 6 min) in 20% (w/w) aqueous solution (\( W_2 \)) of a ternary biopolymer blend (GA66%-MG17%-MD17% w/w), selected because it acts as barrier against oxygen transfer, preventing lipid oxidation, (Pérez-Alonso et al., 2003) and because of their ability to provide long-term stability to \( W_1/O/W_2 \) double emulsions (Vernon-Carter et al., 1998).

2.3 Microencapsulation of \( W_1/O/W_2 \)

The \( W_1/O/W_2 \) double emulsion was fed at a rate of 40 mL/min to a Nichols/Niro spray-drier (Turbo Spray PLA, NY, USA) operated with an inlet temperature of 135 ± 5 °C, outlet temperature at 80 ± 5 °C and injecting compressed air at 4 bar. The spray-dried microcapsules (\( M_{GA} \)) were collected, kept in plastic bags wrapped with aluminium foil and stored in desiccators containing silica gel at room temperature.

2.4 Sorption isotherms of \( M_{GA} \) microcapsules

\( M_{GA} \) microcapsules were put into Petri dishes, covering completely and homogeneously the dishes surface. The dishes were then introduced into glass desiccators containing \( P_2O_5 \) as a desiccant, at room temperature for 3 weeks in order to reduce to a minimum the moisture content (~2%) of the microcapsules. The adsorption isotherms were determined experimentally by the gravimetric method described by Lang et al. (1981) at 20, 35 and 40 (± 0.1) °C in the range of water activity (\( a_w \)) between 0.11 and 0.85 (Labuza et al., 1985). This method was described by Sánchez-Sáenz et al. (2011).

2.5 Sorption models

The models of Caurie and Guggenheim-Anderson-De Boer (GAB) were used to evaluate the behaviour of the equilibrium moisture content (\( M \)) in function of water activity (\( a_w \)). The GAB equation is recognized as the most versatile sorption model available for the sorption of food and has been the base for the determination of thermodynamic functions of microcapsules, as integral enthalpy and integral entropy, used as parameters of stability of food systems (Pérez-Alonso et al., 2006; Bonilla et al., 2010). It is mathematically expressed as Rizvi (1986):

\[
M = \frac{M_{0G} \cdot C_G \cdot K_G \cdot a_w}{(1 - K_G \cdot a_w) \cdot (1 - K_G \cdot a_w + C_G \cdot K_G \cdot a_w)}
\]  

(Caurie equation, Caurie, 2005) is based in unimolecular physical adsorption and was derived from classical BET multimolecular adsorption equation introducing a third parameter into general statements. A linear form for plotting purposes could be expressed as Singh et al. (2006):

\[
\ln \left( \frac{1}{M} \right) = \ln \left( \frac{1}{C_C \cdot C_G \cdot M_{0C}} \right) + 2 C_C \frac{1}{M_{0C}} \ln \left( \frac{1 - a_w}{a_w} \right)
\]  

The models fit to experimental data were estimated using non-linear regression with Origin version 8.5 (OriginLab Corp., Northampton, MA, USA). Goodness of fit was evaluated using the relative percentage difference between the experimental and predicted values of moisture content, or mean relative
deviation modulus (E), defined by the Eq. (3) (McLaughlin and Magee, 1998):

$$E = \frac{100}{n_s} \sum \frac{|M_i - M_E|}{M_i}$$  \hspace{1cm} (3)

It is generally assumed that a good fit is obtained when E < 5%.

2.6 Sorption properties of MGA microcapsules

Caurie equation not only correlates equilibrium moisture content in food systems but also explain different properties of sorbed water (Singh et al., 2006). The Caurie equation predicted that the density of primary or tightly bound molecules is greater than unity and equal to \( C_{C/1/n} \) and this high adsorbate density at low values of \( a_w \) was responsible for the phenomenon of adsorption compression (Caurie, 2005). The Caurie’s plot of ln\((1 - a_w)/a_w\) vs ln\(1/M\) was used to obtain adsorption centers (Caurie, 2005):

$$n = \frac{M_{OC}}{C \cdot C_{C/1/n}}$$  \hspace{1cm} (4)

percent of bound water (Singh et al., 2006):

$$B = M_{OC} \cdot n$$  \hspace{1cm} (5)

and surface area of adsorption (Singh et al., 2006):

$$S = \frac{54.54 \cdot C \cdot C_{C/1/n}}{M_{OC}}$$  \hspace{1cm} (6)

In porous adsorbents the adsorption process involves the filling and transport of molecules in pore channels. Hence, the understanding of adsorption process requires a reliable characterization of pore structure (Sonwane and Bhatia, 2000). Among the important pore characteristics the pore radius is of particular interest since it can be obtained from sorption isotherms. As the adsorptive filling begins to occur, the Kelvin-law effects begin to become significant and the Kelvin equation allows the determination of pore radius. However, the Kelvin equation does not take into account the thickness of layers formed on the porous surface prior to condensation (Rosa et al., 2010). In order to describe the thickness of the precondensation film on the pore walls, 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). Therefore pore radius \( R_p \) is (Singh et al., 2001):

$$R_p = 10^9 \cdot r_c + t$$  \hspace{1cm} (7)

The Kelvin equation was used for the calculation of critical radius \((r_c)\). This equation applies primarily to the condensation region of the isotherm (Singh et al., 2001):

$$r_c = \frac{2\sigma \cdot V_M}{R \cdot T \cdot \ln(1/a_w)}$$  \hspace{1cm} (8)

The Halsey equation was used for the calculation of thickness of the water adsorbed layer (Singh et al., 2001):

$$t = 0.354 \left( \frac{-5}{\ln a_w} \right)^{1/3}$$  \hspace{1cm} (9)

As water is bound by different mechanisms in different water activity regions, in pores below a certain critical size (called as micropores), the pore filling mechanism deviates from the Kelvin-law due to a behaviour dominated by interactions with the adsorbent. In such cases, the Dubinin-Radushkevich model is widely used to consider this micropore filling (Sonwane and Bhatia, 2000; Azuara and Beristain, 2006).

$$\log(M) = \log(M_{OD}) - \log^2 \left( \frac{1}{a_w} \right)$$  \hspace{1cm} (10)

According to the latter model, for low pressures, adsorption in micropores will proceed by volume filling and the mesopores will have a submonolayer region and for higher pressures, in the case of multilayer region, micropores will be filled by capillary condensate while the larger ones will have a multilayer thickness of the adsorbate (Sonwane and Bhatia, 2000).

2.7 Integral enthalpy \((\Delta H_{int})\) and integral entropy \((\Delta S_{int})\) thermodynamic functions of the MGA microcapsules

The determination of the integral (enthalpy and entropy) thermodynamic functions, and the water activity-temperature conditions where the microcapsules minimum integral entropy occurred, considered as the point of maximum storage stability, was established as indicated by Pérez-Alonso et al. (2006) and Bonilla et al. (2010). These authors have provided a thorough description of the procedure followed and equations used for this purpose.
2.8 Enthalpy-Entropy compensation theory

The compensation theory proposes a linear relationship between enthalpy and entropy (McMinn et al., 2004; Azuara and Beristain, 2006; Silveira et al., 2010). Values for $\Delta H_{int}$ and $\Delta S_{int}$ were correlated with the law of compensation:

$$\Delta H_{int} = T\beta\Delta S_{int} + \Delta G\beta$$  (11)

Krug et al. (1976a, 1976b) proposed a statistical analysis test to corroborate the compensation theory. This involves a comparison of $T\beta$ with the harmonic mean temperature ($T_{hm}$), defined as:

$$T_{hm} = \frac{n_i}{\sum \frac{1}{T_i}}$$  (12)

The compensation theory only applies if $T\beta \neq T_{hm}$.

2.9 Statistical analyses

The experimental data were analysed using one-way analysis of variance (ANOVA), and Tukey’s test used for establishing the statistical significance ($P \leq 0.05$), with the help of the SPSS Statistics 19.0 software. All experiments were done in triplicate.

3 Results and discussion

3.1 Sorption isotherms of $M_{GA}$ microcapsules

The experimental sorption isotherms at 20, 35, and 40 °C for $M_{GA}$ microcapsules are shown in Fig. (1) where a type II isotherm according to BET classification (sigmoid shape) was evidenced for all temperatures (Brunauer et al., 1938). Generally, the equilibrium moisture content is expected to decrease with increasing temperature at constant water activity. This trend was observed for $M_{GA}$ microcapsules, where equilibrium moisture content decreased as temperature increased. This could be attributed to the kinetic energy of water molecules, at lower temperatures water molecules have a lower kinetic energy which is not enough to overcome the corresponding sorption energy or a reduction in the number of polar or active sites due to shrinkage where more intense interactions among active sites through hydrogen bonds are developed (Erbas et al., 2005).

3.2 Adsorption properties of $M_{GA}$ microcapsules

Table 1 shows the fitting constants of adsorption models, the determination coefficient ($r^2$) and the mean relative deviation modulus ($E$). The GAB and Caurie models describe adequately the experimental data throughout the range of temperature studied with a mean $E$ value of 2.55% and 2.57%, respectively. Treatments of sorption data according to the GAB equation allow the evaluation of monolayer moisture content values ($M_0C$) of the microcapsules.
The value of the monolayer ($M_{0G}$) is of particular interest, as it indicates the amount of water that is strongly adsorbed to specific sites and is considered as the optimum value at which a food is more stable against microbial spoilage (Pérez-Alonso et al., 2006).

The $M_{0G}$ values of $M_{GA}$ microcapsules diminished as temperature increased from 20 to 40 °C as it happened with the experimental equilibrium moisture contents data. The $M_{0G}$ values obtained for $M_{GA}$ microcapsules from GAB model were between 2.72 and 5.20 kg H$_2$O/100 kg d.s. (Table 1). Similar $M_{0G}$ values were obtain for dried canola oil emulsions (Bonilla et al., 2010) (3.98-5.68 kg H$_2$O/100 kg d.s.), concentrated and freeze dried concentrated yogurts (Azuara and Beristain, 2006) (2.47-4.14 kg H$_2$O/100 kg d.s.). The values of $C_G$ and $K_G$ for $M_{GA}$ microcapsules (Table 1) fell within the range of 5.67 ≤ $C_G$ < ∞ and of 0.24 < $K_G$ ≤ 1, which according to Lewicki (1997) describe properly an isotherm mathematically. The parameter $C_G$ is related to the heat of adsorption of water on the $M_{GA}$ microcapsules. It is assumed that strong adsorbent-adsorbate interactions, which are exothermic, are favoured at lower temperature, causing an increase in parameter $C_G$ with decreasing temperature (Diosady et al., 1996). However, in this work the values of $C_G$ showed an opposite trend with temperature changes. This trend was similar to that obtain by Iglesias and Chirife (1982) who studied more than 30 foods and found that in 74% of them $C_G$ did not decrease as temperature increased, probably due to irreversible changes associated with increasing temperature, such as enzymatic reactions and protein denaturation. GAB constant $K_G$ is a correcting parameter for the properties of the multilayer molecules with respect to bulk liquid. This constant describes the profile of the isotherm at high water activity range, regulating the upswing after the plateau at medium water activity range (Erbas et al., 2005). As temperature increased, $K_G$ values also increased (Table 1) indicating multilayer molecules became more entropic (Diosady et al., 1996). When $K_G$ = 1, the multilayers have bulk liquid properties, therefore at 35 and 40 °C the water molecules are least bound to the $M_{GA}$ microcapsules surface having a negative effect in $M_{GA}$ microcapsules stability. To compensate this negative effect in adsorbent-adsorbate interactions it is necessary to decrease the moisture content as observed in $M_{0G}$. It can also be that both $C_G$ and $K_G$ parameters lack of physical meaning and they just are a result from the mathematical data fit to the model. Since Caurie model is based in monomolecular adsorption, it allows the determination of some characteristics of bound water and the surface where they adsorb. The maximum moisture content that each adsorption centre in the $M_{GA}$ microcapsules surface is capable of attracting ($M_{0C}$) were between 4.64 and 5.59 kg H$_2$O/100 kg d.s. and diminished as temperature increased resembling monolayer moisture content ($M_{0G}$) values of GAB model particularly at 20 °C, but as temperature increase the difference between $M_{0C}$ and $M_{0G}$ also increase. This could be attributed to the difference in the equation form and how parameters compensate each other in the models. Similar values were found for starch (7.45-7.99 kg H$_2$O/100 kg d.s.) and gluten (6.65-7.58 kg H$_2$O/100 kg d.s.) (Caurie, 2005), and raw goat meat (3.55-6.15 kg H$_2$O/100 kg d.s.) (Singh et al., 2006). Unit volumes of space or adsorption centres ($n$) in Caurie model diminished

Table 1. Estimated values of coefficients obtained for sorption models applied to experimental adsorption data for $M_{GA}$ microcapsules

<table>
<thead>
<tr>
<th>Model</th>
<th>Constant</th>
<th>Temperature (°C)</th>
<th>Mean E (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>20</td>
<td>35</td>
</tr>
<tr>
<td>GAB</td>
<td>$M_{0G}$</td>
<td>5.20 ± 0.10&lt;sup&gt;a&lt;/sup&gt;</td>
<td>3.23 ± 0.08&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>$C_G$</td>
<td>8.83 ± 0.28&lt;sup&gt;a&lt;/sup&gt;</td>
<td>17.43 ± 0.50&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>$K_G$</td>
<td>0.76 ± 0.02&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.90 ± 0.03&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>$r^2$</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>$E$</td>
<td>1.06</td>
<td>3.36</td>
</tr>
<tr>
<td>Caurie</td>
<td>$M_{0C}$</td>
<td>5.58 ± 0.21&lt;sup&gt;b&lt;/sup&gt;</td>
<td>5.09 ± 0.20&lt;sup&gt;a,b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>$C_C$</td>
<td>1.04 ± 0.03&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.03 ± 0.04&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>$n$</td>
<td>4.55 ± 0.19&lt;sup&gt;b&lt;/sup&gt;</td>
<td>4.38 ± 0.15&lt;sup&gt;a,b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>$r^2$</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>$E$</td>
<td>3.08</td>
<td>1.81</td>
</tr>
</tbody>
</table>

Values are means ± standard error, of three replicates. Superscripts with different letters in same line indicate significant differences (P ≤ 0.05).
analysed the bound water properties of goat meat finding lesser adsorption centres (2.22-3.09), smaller surface areas (60.51-84.03 m²/g) but higher densities (1.60-1.99 m²/g). This could be attributed to the pore size present in the surface structure of the adsorbent, as smaller is the pore size more bounded are water molecules to the surface. For raw goat meat in the entire range of moisture content studied by Singh et al. (2006) there exist only micropores (< 2 nm).

Pore radius of MGA microcapsules is shown in Table 3. The pore radius (R_p) of MGA microcapsules at the studied moisture contents ranged from 0.67 to 8.15 nm, which can be classified as micropores (M < 3 kg H₂O/100 kg d.s., a_w < 0.24) and mesopores (between 3 and 14 kg H₂O/100 kg d.s., 0.24 < a_w < 0.86) according to the IUPAC classification (Rosa et al., 2010). The pores, in general, enlarged with increase in sorption temperature, this could be attributing to the shrinkage of the biopolymeric matrix. This is in accordance with the properties obtain with Caurie model where the number of adsorption centres (n) decline as the temperature increase (Table 1) and the specific surface area obtained in this work.

Since Kelvin equation is limited for pore sizes around 2 nm, where capillary phenomena lose dominance, the Dubinin-Radushkevich model was used to characterize the micropore region. The Dubinin-Radushkevich parameters for sorption isotherms of MGA microcapsules are shown in Table 4. The moisture contents corresponding to the micropore volume (M_{0D}) were between 2 and 3 kg H₂O/100 kg d.s. that indicates that the formation of the monolayer moisture content occurs after all micropores are filled. As temperature increase M_{0D} decrease probably due to the shrinkage of the biopolymeric matrix of MGA microcapsules or the increase in kinetic energy of water molecules with temperature as mentioned before. Diffusion in micropores is generally known to be dominated by interactions between the diffusing molecule and the pore walls (entropic effects) (Fletcher and Thomas, 2000).

Table 2. Adsorption properties of bound water from Caurie model

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>C^{1/n} (g/cm³)</th>
<th>Bound water (B) (%)</th>
<th>Surface area (S) (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1.23 ± 0.05a</td>
<td>25.46 ± 0.97a</td>
<td>124.23 ± 5.22a</td>
</tr>
<tr>
<td>35</td>
<td>1.16 ± 0.04a</td>
<td>22.27 ± 0.71b</td>
<td>119.35 ± 4.77ab</td>
</tr>
<tr>
<td>40</td>
<td>1.13 ± 0.03a</td>
<td>19.06 ± 0.53a</td>
<td>112.00 ± 3.36a</td>
</tr>
</tbody>
</table>

Values are mean ± standard error, of three replicates. Superscripted with different letters in same column indicate significant differences (P ≤ 0.05).
Table 3. Pore radius (nm) of $M_{GA}$ microcapsules at different temperatures

<table>
<thead>
<tr>
<th>$M$ (kg H$_2$O/100 kg d.s.)</th>
<th>Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20</td>
</tr>
<tr>
<td>1</td>
<td>$0.72 \pm 0.03^a$</td>
</tr>
<tr>
<td>2</td>
<td>$0.87 \pm 0.02^a$</td>
</tr>
<tr>
<td>3</td>
<td>$1.04 \pm 0.03^a$</td>
</tr>
<tr>
<td>4</td>
<td>$1.25 \pm 0.05^a$</td>
</tr>
<tr>
<td>5</td>
<td>$1.51 \pm 0.04^a$</td>
</tr>
<tr>
<td>6</td>
<td>$1.84 \pm 0.07^a$</td>
</tr>
<tr>
<td>7</td>
<td>$2.22 \pm 0.06^a$</td>
</tr>
<tr>
<td>8</td>
<td>$2.68 \pm 0.08^a$</td>
</tr>
<tr>
<td>9</td>
<td>$3.22 \pm 0.10^a$</td>
</tr>
<tr>
<td>10</td>
<td>$3.85 \pm 0.12^a$</td>
</tr>
<tr>
<td>11</td>
<td>$4.60 \pm 0.16^a$</td>
</tr>
<tr>
<td>12</td>
<td>$5.52 \pm 0.14^a$</td>
</tr>
<tr>
<td>13</td>
<td>$6.67 \pm 0.19^a$</td>
</tr>
<tr>
<td>14</td>
<td>$8.15 \pm 0.24^a$</td>
</tr>
</tbody>
</table>

Values are means ± standard error, of three replicates. Superscripts with different letters in same line indicate significant differences (P ≤ 0.05).

Meanwhile, in mesopores (20 Å < pore diameter < 50 Å), surface forces and capillary forces become important, whereas for the macropores (pore diameter > 50 Å), very little is contributed by the pore characteristics to the adsorption capacity (Azuara and Beristain, 2006).

### 3.3 Integral enthalpy ($\Delta H_{int}$) and integral entropy ($\Delta S_{int}$) thermodynamic functions of the $M_{GA}$ microcapsules

The variation in integral enthalpy $\Delta H_{int}$ with moisture content indicates the level to which water-microcapsule interaction is greater than the interaction of water molecules. Fig. 2 shows that the integral enthalpy increased to a maximum with increasing moisture content, and then gradually decreased in magnitude with further increase in moisture content in the same range of temperature studied. The low enthalpy values, at low moisture content, are an indication of the occupation of highly accessible sites on the microcapsule surface. Moreover, as the moisture content increased the binding of water at higher energy sites (stronger binding) was reflected in the increase in enthalpy. The maximum enthalpy value indicates the covering of the strongest binding sites and the greatest water-microcapsule interaction. The covering of less favourable locations and the formation of multi-layers then follows, as shown by the decrease in enthalpy with increasing moisture content. The values of the equilibrium moisture content corresponding to the maximum equilibrium

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Fig. 2. Integral enthalpy as a function of moisture content of $M_{GA}$ microcapsules.

Fig. 3. Integral entropy as a function of moisture content of $M_{GA}$ microcapsules.
heat of sorption (~24.20 kJ/mol) were close to the values found for the monolayer moisture content estimated by the GAB model (Table 1). For the temperatures of 20, 35 and 40 °C there were 3.61, 3.65 and 3.81 kg H₂O/100 kg d.s., respectively (Fig. 2). These results are consistent, because monolayer moisture content indicates the amount of water is strongly adsorbed at specific sites and to break these bonds maximum energy is required compared to other moisture contents. A similar relationship between net integral enthalpy and moisture content was reported for potatoes (McMinn and Magee, 2003), freeze-dried yogurts and concentrated yogurts (Azuara and Beristain, 2006) and rosemary essential oil microcapsules (Silva et al., 2014).

Fig. (3) shows the integral entropy as a function of moisture content at 20, 35 and 40 °C. The microcapsules showed a decrease in integral entropy reaching a minimum and then increasing in magnitude as moisture content increased. The decrease in integral entropy represents an increase in the restriction of water molecules mobility as available sites become saturated and higher energy sites are utilized; the subsequent increase implies that water molecules are free to form multilayers. At higher moisture contents, entropy will be approximately the same as liquid water (McMinn and Magee, 2003). The minimum integral entropy is considered as that of maximum stability because it is where water molecules achieve a more ordered arrangement within the solid (microcapsule) and strong bonds between the adsorbate and the adsorbent occur, thus, water is less available to participate in spoilage reactions (Nunes and Rotstein, 1991; Pérez-Alonso et al., 2006). The conditions for maximum stability of microcapsules were obtained from the analysis of ΔS_int, a_w, and M conditions related to the minimum point (Table 4). As temperature increased the moisture content and water activity in the microcapsules increased. Further, the integral entropy can be directly related to the order-disorder of water molecules sorbed on microcapsule, and therefore is a useful function to study the effect of drying method on the stability of the product (Azuara and Beristain, 2006). Silva et al. (2014) determined the maximum stability conditions for rosemary essential oil microencapsulated using gum Arabic as wall material obtained by spray drying and found that the highest stability occurred at values of water activity of 0.358, 0.292, 0.250 and 0.119 in relation to temperatures over 15, 25, 35 and 40 °C.

### 3.4 Enthalpy-entropy compensation

Enthalpy-entropy compensation theory or isokinetic compensation theory is used to evaluate physical and chemical phenomena such as sorption reactions. This theory allows one to check whether there will be greater molecular interaction due to freedom reduction or to the link of the molecules in the food, generating larger organization or order (related to enthalpy) over disorganization and greater freedom of the molecules in the food (related to entropy) (Spada et al., 2013). The theory only applies if the isokinetic temperature (T_β) is different from the harmonic mean temperature (T_{hm}) (Krug et al., 1976a; Krug et al., 1976b). Fig. (4) shows the enthalpy-entropy compensation obtained by plotting the integral properties. The arrowheads indicate the direction of adsorption from lowest to highest moisture equilibrium. As can be seen, the microcapsules presented two lines. The first at low moisture contents, with T_β1 = 277.20 ± 5.31 K at 20 °C (0-3.61 kg H₂O/100 kg d.s.), T_β1 = 279.23 ± 1.80 K at 35 °C (0-3.65 kg H₂O/100 kg d.s.) and T_β1 = 276.20 ± 4.00 K at 40 °C (0-3.81 kg H₂O/100 kg d.s.). The second line, which covers the rest of the moisture range studied, with T_β2 = 346.68 ± 6.64 K at 20 °C, T_β2 = 349.59 ± 6.36 K at 35 °C and T_β2 = 345.37 ± 2.03 K at 40 °C. These values were obtained by fitting the data with the equation 18, which presented coefficients of determination (r²) up to 0.99, indicating that compensation existed. The isokinetic theory can be confirmed because the mean harmonic temperature (T_{hm}) corresponded to 304.58 K, and this value was different from T_β.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>M_{0D} (kg H₂O/100 kg d.s.)</th>
<th>b</th>
<th>r²</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>3.06 ± 0.12⁰</td>
<td>0.62 ± 0.02⁰</td>
<td>0.96</td>
</tr>
<tr>
<td>35</td>
<td>2.48 ± 0.07⁰</td>
<td>0.67 ± 0.03⁰</td>
<td>0.99</td>
</tr>
<tr>
<td>40</td>
<td>2.05 ± 0.09⁰</td>
<td>0.73 ± 0.03⁰</td>
<td>0.99</td>
</tr>
</tbody>
</table>

Values are means ± standard error, of three replicates. Superscripts with different letters in same column indicate significant differences (P ≤ 0.05).
Moreover, the values of moisture content where may be considered as mainly enthalpy-driven.

According to Leffler (1955), it can be postulated that from very low moisture up to values prior to the minimum integral entropy the sorption process of water molecules is entropy driven \((T_β < T_{\text{hom}})\); at the point of minimum integral entropy, there is an equilibrium between entropy and enthalpy mechanisms; and after minimum integral entropy, enthalpy controls the sorption process of water molecules \((T_β > T_{\text{hom}})\). This explains why in this work the sorption process of water molecules was entropy driven at low moisture contents because of micropores were predominant and as pores increased to mesopore sizes the process became enthalpy driven.

Therefore, water sorption in \(M_{GA}\) microcapsules may be considered as mainly enthalpy-driven. Moreover, the values of moisture content where minimum \(ΔS_{\text{int}}\) appeared were closed to the moisture contents corresponding to the micropore volume (\(M_{(0p)}\)) indicating that maximum stability conditions are closely related with the micropore structure of \(M_{GA}\) microcapsules. Azuara and Beristain (2006) found similar results for different yogurts and stated that the adsorption process was controlled by entropy when the water molecules were adsorbed in the micropores and was controlled by enthalpy when the water molecules were adsorbed in the mesopores and macropores. The free energy change \(ΔG_β\) is an indicative of the affinity adsorbate-adsorbent and provide us a criterion to whether water sorption is a spontaneous \((-ΔG_β)\) or non-spontaneous \((+ΔG_β)\) process. In this work \(ΔG_β\) was between -5.66 and -5.40 kJ/mol at moisture contents between 0.381 kg H2O/100 kg d.s. and between -0.51 and -0.49 kJ/mol at moisture contents higher than 3.81 kg H2O/100 kg d.s., for temperatures of 20, 35 and 40 °C indicating that entropic and enthalpic mechanisms of moisture adsorption are spontaneous processes in \(M_{GA}\) microcapsules.

**Conclusions**

The adsorption isotherms of the microcapsules presented a sigmoidal shape common to most food materials. At all \(a_W\) levels, the equilibrium moisture contents decreased with increase in temperature. The GAB equation was useful for modelling moisture sorption of the microcapsules in a water activity range of 0.11-0.85 and at 20, 35 and 40 °C. The pore radius of the microcapsules presented values in the range from 0.67 to 8.15 nm increasing as moisture content and temperature increase and they are classified as micropores and mesopores. The minimum integral entropy is proposed as indicative of the most suitable conditions for storage, with the corresponding \(a_W\) being available from the isotherm; this is in the range of 0.19-0.37 for the temperature range between 20 and 40 °C. The enthalpy-entropy compensation theory suggest that the adsorption processes in the microcapsules are entropy driven at low moisture contents up to values prior to the minimum integral entropy and after that, the sorption process is enthalpy driven.

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**Nomenclature**

\(a_W\) water activity  
\(S\) surface area of adsorption (m²/g)  
\(b\) constant related to the microporous structure of the adsorbent in Dubinin-Radushkevich model  
\(B\) percent of bound water  
\(C_C\) constant related to the BET monolayer moisture content in Caurie model  
\(C_G\) Guggenheim coefficient in GAB model  
\(E\) mean relative deviation modulus
$K_G$ coefficient correcting properties of the multilayer molecules with respect to the bulk liquid in GAB model
$m$ number of ($\Delta H_{int}$, $\Delta S_{int}$) data pairs
$M$ equilibrium moisture content (kg water/100 kg dry solids)
$M_{GA}$ microcapsules moisture content of the nutraceutical system
$M_{Ei}$ the predicted moisture content at observation $i$
$M_i$ the moisture content at observation $i$
$M_{0C}$ maximum moisture content (kg water/100 kg dry solids) that each adsorption centre is capable of attracting in Caurie model
$M_{0D}$ amount of moisture adsorbed (kg water/100 kg dry solids) corresponding to the micropore volume in Dubinin-Radushkevich model
$M_{0G}$ monolayer water content (kg water/100 kg dry solids) in GAB model
$n$ number of adsorption centres on the unimolecular surface in Caurie model
$n_i$ total number of isotherms used
$n_s$ number of observations
$R$ universal gas constant (kJ/mol K)
$R_p$ pore radius (nm)
$r_c$ critical radius (m)
$t$ multilayer thickness (nm)
$T_{hm}$ harmonic mean temperature (K)
$T_B$ isokinetic temperature (K)
$V_M$ molal volume of sorbate (m$^3$/mol)

Greek symbols
$\Delta G_B$ free energy at $T_B$ (kJ/mol)
$\Delta H_{int}$ molar integral enthalpy (kJ/mol K)
$\sigma$ surface tension (N/m)
$\Delta S_{int}$ molar integral entropy (kJ/mol K)

References


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