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MOISTURE SORPTION PROPERTIES AND STORAGE STABILITY CONDITIONS OF A NUTRACEUTICAL SYSTEM MICROENCAPSULATED BY SPRAY DRYING
PROPIEDADES DE ADSORCIÓN DE HUMEDAD Y CONDICIONES DE ESTABILIDAD EN ALMACENAMIENTO DE UN SISTEMA NUTRACÉUTICO MICROENCAPSULADO POR SECADO POR ASPERSIÓN

L.M.A. Pavón-García¹, R. Gallardo-Rivera², A. Román-Guerrero², H. Carrillo-Navas^{1,3}, M.E. Rodríguez-Huezo⁴,
A.Y. Guadarrama-Lezama¹, C. Pérez-Alonso*

¹Facultad de Química, Universidad Autónoma del Estado de México, Paseo Colón esq. Paseo Tollocan s/n, Col. Residencial Colón, C.P. 50120, Toluca, Estado de México, México.

²Departamento de Biotecnología, Universidad Autónoma Metropolitana-Iztapalapa, San Rafael Atlixco No. 186, Col. Vicentina, C.P. 09340, México, D.F., México.

³Departamento de Ingeniería de Procesos e Hidráulica, Universidad Autónoma Metropolitana-Iztapalapa, San Rafael Atlixco No. 186, Col. Vicentina, C.P. 09340, México, D.F., México.

⁴Departamento de Ingeniería Química y Bioquímica, Tecnológico de Estudios Superiores de Ecatepec, Estado de México, México.

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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 isotermas de adsorción de un sistema nutracéutico microencapsulado por secador por aspersión, a 20, 35 y 40°C. Los datos experimentales de las isotermas 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: isotermas de adsorción, radio de poro, mínimo de entropía integral, compensación entalpía-entropía, actividad de agua.

* Corresponding author. E-mail: cpereza@uaemex.mx
Phone: +52 722 2173890; Fax: +52 722 2175109

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-Higueta *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 tartaric 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 Potosi 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, MaltadexTM 10) 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 de Mexico, S.A. de C.V., Mexico City, Mexico) was used as preservative.

2.2 Formulation and preparation of double W₁/O/W₂ emulsion

A water-in-oil-in-water double emulsion (W₁/O/W₂) was prepared at room temperature (25 ± 1 °C) using a two-stage emulsification procedure. In the first stage, a W₁/O emulsion was formulated with a 0.5 dispersed phase mass fraction. Total emulsifier concentration in W₁/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 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 W₁/O primary emulsion was re-emulsified (7600 rpm for 6 min) in 20% (w/w) aqueous solution (W₂) 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 W₁/O/W₂ double emulsions (Vernon-Carter *et al.*, 1998).

2.3 Microencapsulation of W₁/O/W₂

The W₁/O/W₂ 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 P₂O₅ 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):

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

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):

$$\ln\left(\frac{1}{M}\right) = \ln\left(\frac{1}{C_C^{1/n} \cdot M_{0C}}\right) + \frac{2C_C^{1/n}}{M_{0C}} \ln\left(\frac{1 - a_w}{a_w}\right) \quad (2)$$

The models fitness 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 Ec. (3) (McLaughlin and Magee, 1998):

$$E = \frac{100}{n_s} \sum \frac{|M_i - M_{Ei}|}{M_i} \quad (3)$$

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

2.6 Sorption properties of M_{GA} 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):

$$n = \frac{M_{0C}}{C_C^{1/n}} \quad (4)$$

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

$$B = M_{0C} \cdot n \quad (5)$$

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

$$S = \frac{54.54 \cdot C_C^{1/n}}{M_{0C}} \quad (6)$$

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):

$$R_p = 10^9 \cdot r_C + t \quad (7)$$

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):

$$r_C = \frac{2\sigma \cdot V_M}{R \cdot T \cdot \ln(1/a_w)} \quad (8)$$

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

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

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).

$$\log(M) = \log(M_{0D}) - b \log^2 \left(\frac{1}{a_w} \right) \quad (10)$$

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 (ΔH_{int}) and integral entropy (ΔS_{int}) thermodynamic functions of the M_{GA} 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 ΔH_{int} and ΔS_{int} were correlated with the law of compensation:

$$\Delta H_{int} = T_{\beta} \Delta S_{int} + \Delta G_{\beta} \quad (11)$$

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

$$T_{hm} = \frac{n_i}{\sum_1^{n_i} (1/T)} \quad (12)$$

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

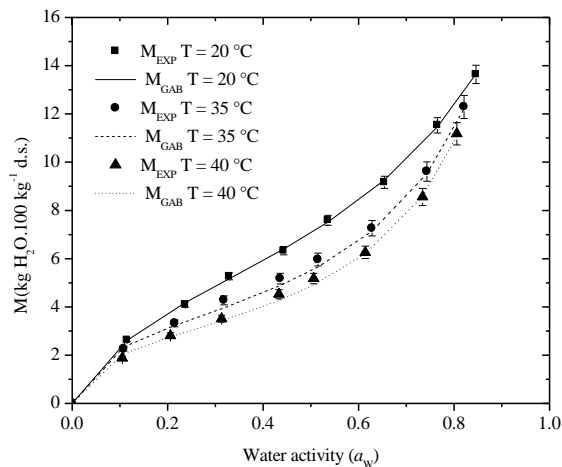
2.9 Statistical analyses

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.

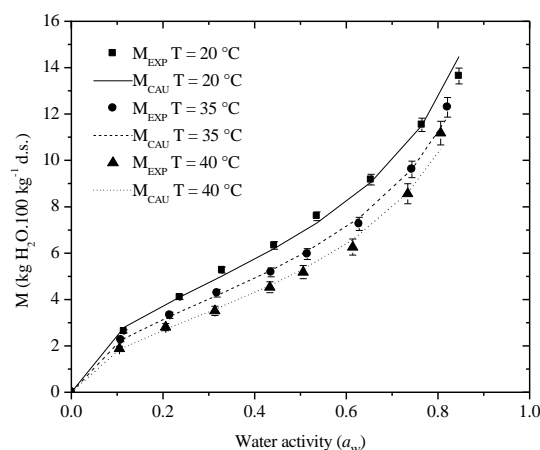
3 Results and discussion

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 (Erbaş *et al.*, 2005).



(a)



(b)

Fig. 1. Experimental sorption isotherms (M_{exp}) of M_{GA} microcapsules at 20, 35 and 40 °C and estimated curves with (a) GAB model (M_{GAB}) and (b) Caurie model (M_{CAU}).

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_{0G}) of the microcapsules.

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

Model	Constant	Temperature (°C)			Mean E (%)
		20	35	40	
GAB	M_{0G}	5.20 ± 0.10^c	3.23 ± 0.08^b	2.72 ± 0.07^a	
	C_G	8.83 ± 0.28^a	17.43 ± 0.50^b	19.00 ± 0.48^c	
	K_G	0.76 ± 0.02^a	0.90 ± 0.03^b	0.94 ± 0.04^b	
	r^2	0.99	0.99	0.99	
	E	1.06	3.36	3.23	2.55
Caurie	M_{0C}	5.58 ± 0.21^b	$5.09 \pm 0.20^{a,b}$	4.64 ± 0.18^a	
	C_C	1.04 ± 0.03^a	1.03 ± 0.04^a	1.03 ± 0.05^a	
	n	4.55 ± 0.19^b	$4.38 \pm 0.15^{a,b}$	4.11 ± 0.12^a	
	r^2	0.99	0.99	0.99	
	E	3.08	1.81	2.81	2.57

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

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 H₂O/100 kg d.s. (Table 1). Similar M_{0G} values were obtained for dried canola oil emulsions (Bonilla *et al.*, 2010) (3.98-5.68 kg H₂O/100 kg d.s.), concentrated and freeze dried concentrated yogurts (Azua and Beristain, 2006) (2.47-4.14 kg H₂O/100 kg d.s.). The values of C_G and K_G for M_{GA} microcapsules (Table 1) fell within the range of $5.67 \leq C_G < \infty$ and of $0.24 < K_G \leq 1$, 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 obtained 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 (Erbaş *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 H₂O/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 H₂O/100 kg d.s.) and gluten (6.65-7.58 kg H₂O/100 kg d.s.) (Caurie, 2005), and raw goat meat (3.55-6.15 kg H₂O/100 kg d.s.) (Singh *et al.*, 2006). Unit volumes of space or adsorption centres (n) in Caurie model diminished

as temperature arise (Table 1) indicating that M_{GA} microcapsules surface presented structural changes with the temperature where active sites were disable for adsorption of water molecules. The complex parameter $C^{1/n}$ (Table 2) represent the weight of primary adsorbate molecules per unit volume of space and it can be considered as the density of strongly bound primary adsorbate molecules (Caurie, 2005). In Table 2 it is noticed that density of bound water is higher than that of pure water (approximately 1 g/cm³ at 20-40 °C), that is because once the water molecules are adsorbed their molecular motion diminish and water molecules occupied lesser volume increasing its density (adsorption compression) (Caurie, 2005). Hence Caurie density ($C^{1/n}$) could be a measure of adsorbent-adsorbate interactions. Higher the adsorbent-adsorbate interactions higher the density, therefore stronger bound. As temperature promotes molecular motion it is expected that density decrease with temperature rising. Since the parameter CC remains practically constant at the temperature range studied (Table 1), the density of bound water in M_{GA} microcapsules depends mainly on the entropic effects due to changes in M_{GA} microcapsules surface (n). The unimolecularly adsorbed molecules at the active centres or in the unit volumes of space may be differentiated on the basis of their binding energy and packing conditions. Molecules adsorbed on the most energetic sites at the active centres may be referred to as strongly bound primary molecules while molecules held on less energetic sites are seen as weakly bound secondary molecules (Caurie, 2005).

Bound water percentage (B) refers to strongly bound primary molecules and, as happens with density, the bound water decrease with temperature (Table 2). The specific surface area values for M_{GA} microcapsules are exhibited in Table 2. The calculated surface area was in the range commonly obtained for food products of 100-200 m²/g (Labuza, 1968). Large surface area of many foodstuffs is due to the existence of an intrinsic microspore structure in these materials (Calzetta-Resio *et al.*, 2000). Singh *et al.* (2006)

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 M_{GA} microcapsules is shown in Table 3. The pore radius (R_p) of M_{GA} 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 M_{GA} 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 M_{GA} 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

T (°C)	$C^{1/n}$ (g/cm ³)	Bound water (B) (%)	Surface area (S) (m ² /g)
20	1.23 ± 0.05 ^a	25.46 ± 0.97 ^c	124.23 ± 5.22 ^b
35	1.16 ± 0.04 ^a	22.27 ± 0.71 ^b	119.35 ± 4.77 ^{a,b}
40	1.13 ± 0.03 ^a	19.06 ± 0.53 ^a	112.00 ± 3.36 ^a

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

Table 3. Pore radius (nm) of M_{GA} microcapsules at different temperatures

M (kg H ₂ O/100 kg d.s.)	Temperature °C		
	20	35	40
1	0.72 ± 0.03 ^a	0.67 ± 0.02 ^a	0.68 ± 0.02 ^a
2	0.87 ± 0.02 ^a	0.84 ± 0.03 ^a	0.88 ± 0.01 ^a
3	1.04 ± 0.03 ^a	1.10 ± 0.04 ^a	1.23 ± 0.02 ^b
4	1.25 ± 0.05 ^a	1.46 ± 0.04 ^b	1.68 ± 0.03 ^c
5	1.51 ± 0.04 ^a	1.90 ± 0.03 ^b	2.16 ± 0.06 ^c
6	1.84 ± 0.07 ^a	2.36 ± 0.06 ^b	2.66 ± 0.05 ^c
7	2.22 ± 0.06 ^a	2.86 ± 0.05 ^b	3.18 ± 0.04 ^c
8	2.68 ± 0.08 ^a	3.39 ± 0.07 ^b	3.72 ± 0.07 ^c
9	3.22 ± 0.10 ^a	3.96 ± 0.08 ^b	4.28 ± 0.09 ^c
10	3.85 ± 0.12 ^a	4.58 ± 0.13 ^b	4.87 ± 0.14 ^b
11	4.60 ± 0.16 ^a	5.24 ± 0.15 ^b	5.48 ± 0.18 ^b
12	5.52 ± 0.14 ^a	5.96 ± 0.19 ^b	6.13 ± 0.12 ^b
13	6.67 ± 0.19 ^a	6.76 ± 0.22 ^a	6.82 ± 0.17 ^a
14	8.15 ± 0.24 ^a	7.63 ± 0.26 ^a	7.54 ± 0.23 ^a

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

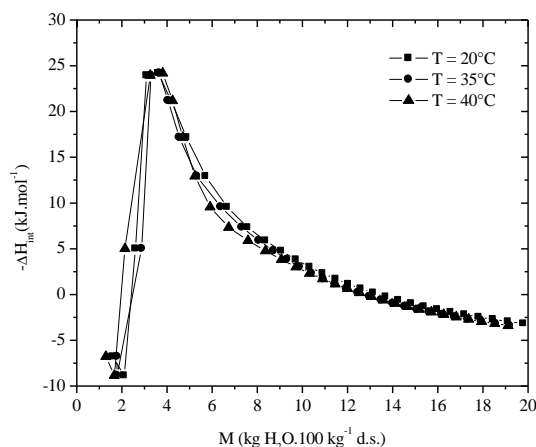


Fig. 2. Integral enthalpy as a function of moisture content of M_{GA} microcapsules.

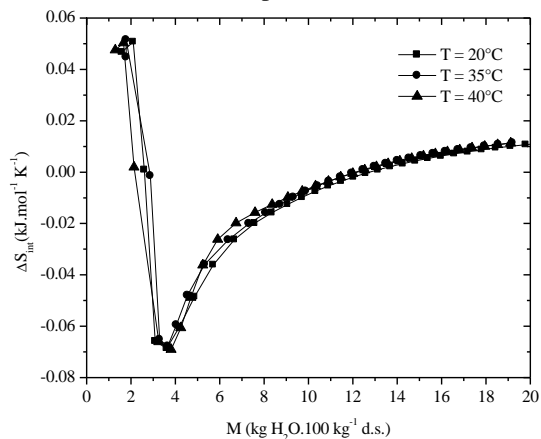


Fig. 3. Integral entropy as a function of moisture content of M_{GA} microcapsules.

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

3.3 Integral enthalpy (ΔH_{int}) and integral entropy (ΔS_{int}) thermodynamic functions of the M_{GA} microcapsules

The variation in integral enthalpy ΔH_{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

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 $T_{\beta 1} = 277.20 \pm 5.31$ K at 20 °C (0-3.61 kg H₂O/100 kg d.s.), $T_{\beta 1} = 279.23 \pm 1.80$ K at 35 °C (0-3.65 kg H₂O/100 kg d.s.) and $T_{\beta 1} = 276.20 \pm 4.00$ 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 $T_{\beta 2} = 346.68 \pm 6.64$ K at 20 °C, $T_{\beta 2} = 349.59 \pm 6.36$ K at 35 °C and $T_{\beta 2} = 345.37 \pm 2.03$ K at 40 °C. These values were obtained by fitting the data with the equation 18, which presented coefficients of determination (r^2) 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 4. Dubinin-Radushkevich parameters for sorption isotherms of M_{GA} microcapsules.

Temperature (°C)	M_{0D} (kg H ₂ O/100 kg d.s.)	b	r^2
20	3.06 ± 0.12^c	0.62 ± 0.02^a	0.96
35	2.48 ± 0.07^b	$0.67 \pm 0.03^{a,b}$	0.99
40	2.05 ± 0.09^a	0.73 ± 0.03^b	0.99

Values are means \pm standard error, of three replicates. Superscripts with different letters in same column indicate significant differences ($P \leq 0.05$).

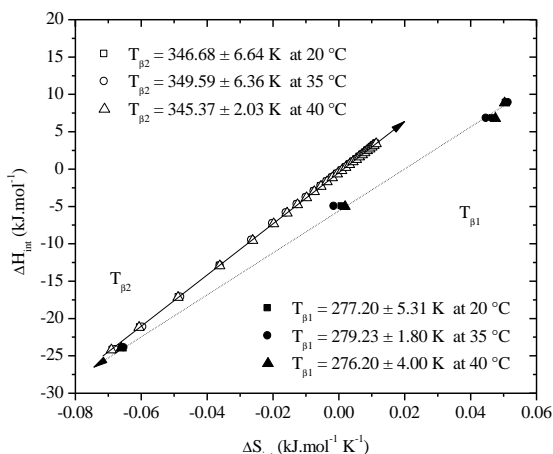


Fig. 4. Integral enthalpy-integral entropy compensation for moisture sorption in M_{GA} microcapsules.

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 ($T_{\beta} < T_{hm}$); 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 ($T_{\beta} > T_{hm}$). 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_{int} appeared were closed to the moisture contents corresponding to the micropore volume (M_{0D}) 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 ($-\Delta G_{\beta}$) or non-spontaneous ($+\Delta G_{\beta}$) process. In this work ΔG_{β} was between -5.66 and -5.40 kJ/mol at moisture contents between 0-3.81 kg $H_2O/100$ kg d.s. and between -0.51 and -0.49

kJ/mol at moisture contents higher than 3.81 kg $H_2O/100$ 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 (m^2/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 (ΔH_{int} , ΔS_{int}) data pairs
M	equilibrium moisture content (kg water/100 kg dry solids)
M_{GA}	microcapsules 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_β	isokinetic temperature (K)
V_M	molal volume of sorbate (m ³ /mol)
<i>Greek symbols</i>	
ΔG_β	free energy at T_β (kJ/mol)
ΔH_{int}	molar integral enthalpy (kJ/mol K)
σ	surface tension (N/m)
ΔS_{int}	molar integral entropy (kJ/mol K)

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