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Water adsorption in rosemary essential oil microparticles: Kinetics, thermodynamics and storage conditions



Eric Keven Silva^{*}, Regiane Victória de Barros Fernandes, Soraia Vilela Borges, Diego Alvarenga Botrel, Fabiana Queiroz

Food Science Department, Federal University of Lavras, Lavras, MG, Brazil

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ABSTRACT

The water adsorption kinetics of rosemary essential oil microparticles encapsulated with gum arabic by spray drying was determined by the static method at 15 °C, 25 °C, 35 °C and 45 °C. The isotherm parameters adjusted by the GAB mathematical model were used to calculate the differential and integral thermodynamic properties, and prediction of the most stable microparticle storage conditions. The mechanisms that direct water vapor adsorption by the theoretical study of enthalpy–entropy compensation were also evaluated. The product reached the equilibrium phases from 144 h of storage and the temperature increase from 15 °C to 45 °C reduced the adsorptive capacity. The Gibbs free energy was negative under all conditions, indicating that the adsorption phenomenon is a spontaneous process. The minimum values for the net integral entropy were indicative of maximum product stability conditions, corresponding to water activities of 0.358–0.119 for the temperature range of 15–45 °C. Isokinetic compensation was confirmed for the adsorption phenomenon and the approach resulted in two zones. At low moisture content the process was controlled by entropy, that is, barriers which limit the water molecules in the product microstructure are more important than the energy of the interactions related to the chemical composition of the microparticles, and at the intermediate-high moisture content, the process was controlled by enthalpy.

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1. Introduction

The essential oil of rosemary (*Rosmarinus officinalis* L.), extracted by hydrodistillation, has been characterized as having antibacterial, antioxidant and free radical scavenger properties (Gachkar et al., 2007), and its use is of great interest to the industry. Gum arabic is one of the most common wall materials used for encapsulating essential oils because of the high encapsulation efficiency (Gharsallaoui et al., 2007). The microencapsulation can be used for many applications in the food industry, including stabilization of the encapsulated material, oxidative reaction control, controlled release delivery, and masking of flavors, colors and odors, thus extending shelf life and protecting the components (Anal and Singh, 2007). One of the most commonly used methods in the microencapsulation process is spray drying.

The physical, chemical and microbiological stability of food depends on the water content and its interaction with the food components. The water adsorption isotherm models the water activity and corresponding moisture content to a constant temperature. The data determined from sorption isotherms help evaluate the storage stability and are also used in the process design and control (Mrad et al., 2012). The moisture sensitivity assessment of dehydrated food products, as well as their hygroscopicity, can be determined through adsorption kinetics, which shows the relationship between increased water content and storage time. The shapes of the adsorption kinetics curves depend on the composition of the powdered product and properties such as temperature and relative humidity of the surrounding environment (Arslan and Toğrul, 2005).

The study of the water adsorption thermodynamics in dehydrated products has attracted great interest because it provides a more thorough interpretation of the sorption isotherm phenomenon and assists in understanding the mechanism (Beristain et al., 2002). According to Bonilla et al. (2010), although the water activity (a_w) and glass transition (T_g) are widely used to predict the shelf

^{*} Corresponding author. Address: Food Science Department, Federal University of Lavras, 3037, zip code 37200-000, Lavras Minas Gerais, Brazil. Tel.: +55 19 98283 3762.

E-mail address: engerickeven@gmail.com (E.K. Silva).

life of food, currently the problem of food product stability should be approached from a new perspective.

The water vapor sorption thermodynamics may propose a reliable scientific criteria for the prediction of the stability and storage life of dehydrated foods. The literature presents several research reports in which sorption thermodynamics has been used as a useful tool to predict the maximum stability conditions for dehydrated foods (Azuara and Beristain, 2006; Beristain et al., 2002; Bonilla et al., 2010; Kaya and Kahyaoglu, 2007; Pérez-Alonso et al., 2006; Rizvi and Benado, 1984; Sánchez-Sáenz et al., 2011; Viganó et al., 2012).

This work aimed to evaluate the kinetics and adsorption phenomena of water vapor in the rosemary essential oil microparticles by calculating the differential and integral thermodynamic properties to predict the best storage and stability conditions of the product and to determine the mechanisms that direct adsorption in the microparticles through the study of enthalpy–entropy compensation.

2. Material and methods

2.1. Material

The rosemary essential oil microparticles used in this study were obtained using a spray dryer (model MSD 1.0, Labmaq Brazil, Ribeirão Preto, Brazil), equipped with a two-fluid atomizer nozzle, using gum arabic as wall material (Colloides Naturels Brasil, São Paulo, Brasil) at a concentration of 19.3%, feed flow rate of 0.92 L h⁻¹ and inlet air temperature of 171 °C. The process conditions were optimized through a previous study by Fernandes et al. (2013).

2.2. Moisture adsorption isotherms

The adsorption isotherms of the microparticles was determined by the static method using saturated salt solutions at 15 °C, 25 °C, 35 °C and 45 °C. The study involved seven saturated salt solutions (LiCl, MgCl, K₂CO₃, NaNO₃, Mg(NO₃)₂, NaCl and KCl) at different temperatures, with water activity ranging from 0.113 to 0.843. The GAB mathematical model (Eq. (1)) showed higher accuracy in describing the adsorption isotherms for all temperatures (Fernandes et al., 2013) and was therefore used as a basis for the calculation of the differential and integral thermodynamic properties of the rosemary essential oil microparticles (Table 1).

$$X_{eq} = \frac{X_m C K a_w}{(1 - K a_w)(1 - K a_w + C K a_w)} \quad (1)$$

X_{eq} : equilibrium moisture content (g water 100 g⁻¹ dry powder); X_m : monolayer moisture content (g water 100 g⁻¹ dry powder); a_w : water activity (dimensionless); C , K : model constants related to monolayer and monolayer properties.

Table 1
Model parameters for GAB isotherms of rosemary essential oil microparticles.

Parameters	Temperature (°C)			
	15	25	35	45
X_m	12.418	11.521	10.286	8.412
K	0.761	0.741	0.768	0.854
C	16.653	23.255	26.681	81.613
R^2	0.999	0.991	0.997	0.997
E	2.047	4.658	2.039	2.215

X_m : monolayer moisture content (g water 100 g⁻¹ dry powder); C , K : model constants related to monolayer and monolayer properties; E : mean relative deviation modulus (%); R^2 : coefficient of determination.

2.3. Thermodynamic properties of adsorption

The procedures for calculating the thermodynamic properties assume that water adsorption is a process that occurs in an inert solid, because equilibrium between the water molecules adsorbed on the solid, and the surrounding water molecules in vapor state is reached. Furthermore, it is considered that the water vapor has an ideal gas behavior, since the process is evaluated at low pressure and that only water adsorption (physisorption) occupies the solid surface (Liebanes et al., 2006).

The differential and integral thermodynamic properties of the rosemary essential oil microparticles were calculated using the methodology proposed by Beristain et al. (1994). The free energy (ΔG) related to the water adsorption phenomenon was calculated using the Gibbs equation (Iglesias et al., 1976):

$$\Delta G = RT \ln(a_w) \quad (2)$$

T : absolute temperature (K); R : universal gas constant (J mol⁻¹ K⁻¹); a_w : water activity (dimensionless).

2.3.1. Differential properties

Variations in the differential molar enthalpy between the water and the wall material of the rosemary essential oil microparticles were determined using the Othmer equation (Othmer, 1940):

$$\frac{d \ln P_v}{d \ln P_v^0} = \frac{(H_v^{dif})_T}{(H_v^0)_T} \quad (3)$$

where the substance adsorbed is water vapor; P_v : water vapor pressure over the adsorbent (Pa); P_v^0 : pressure of vapor of pure water at the sorption temperature (Pa); $H_v^{dif}(T)$: total differential isosteric heat of water adsorption or total differential enthalpy of water adsorption (J mol⁻¹); $H_v^0(T)$: enthalpy of condensation of pure water (J mol⁻¹).

All terms are temperature dependent, so the equation can be integrated to the equilibrium moisture content (X_{eq}) constant:

$$\ln(P_v) = \left(\frac{H_v^{dif}(T)}{H_v^0(T)} \right)_{X_{eq}} \ln(P_v^0) + C_1 \quad (4)$$

where C_1 is an adsorption constant resulting from the integration of Eq. (3).

The values of H_v^0 as a function of temperature can be obtained from tables of pure water or steam through Eq. (5) (Wexler, 1976):

$$H_v^0(T) [\text{J mol}^{-1}] = 6.15 \times 10^4 - 94.14 \times T + 17.74 \times 10^{-2} T^2 - 2.03 \times 10^{-4} T^3 \quad (5)$$

If the relationship between the studied temperatures is kept constant, the graph of $\ln(P_v)$ versus $\ln(P_v^0)$ results in a linear function, whose slope numerically represents the relationship of $H_v^{dif}(T)$ and $H_v^0(T)$.

The net differential isosteric heat or net differential enthalpy (ΔH_{dif}) is defined by:

$$(\Delta H_{dif})_T = \left(\frac{H_v^{dif}(T)}{H_v^0(T)} - 1 \right)_{X_{eq}} H_v^0(T) \quad (6)$$

Calculating $H_v^{dif}(T)$ $H_v^0(T)$ by using Eq. (5), and substituting it into Eq. (7), it is possible to estimate the ΔH_{dif} at different temperatures using pure water steam tables.

With the values obtained for ΔH_{dif} , the variation of the differential entropy (ΔS_{dif}) can be calculated by the Gibbs–Helmholtz equation:

$$\Delta G = (\Delta H_{dif})_T - T(\Delta S_{dif})_T \quad (7)$$

Substituting Eq. (2) in Eq. (7) and rearranging, it follows:

$$(S_{dif})_T = S_1 - S_L = \frac{-(\Delta H_{dif})_T - RT \ln(a_w)}{T} \quad (8)$$

where $S_1 = (\partial S / \partial N_1)_{T,p}$: differential molar entropy of water adsorbed on microparticles ($\text{J mol}^{-1} \text{K}^{-1}$); S_L : molar entropy of pure water in equilibrium with the vapor ($\text{J mol}^{-1} \text{K}^{-1}$); S_1 : total entropy of water adsorbed on microparticles ($\text{J mol}^{-1} \text{K}^{-1}$); N_1 : number of moles of water adsorbed on microparticles.

2.3.2. Integral properties

The net integral enthalpy (ΔH_{int}) of the rosemary essential oil microparticles was calculated using an expression similar to that used for calculating the ΔH_{dif} , but instead of keeping the moisture content constant, the calculations were performed keeping the diffusion pressure constant (ϕ):

$$(\Delta H_{int})_T = \left(\frac{H_v^{int}(T)}{H_v^0(T)} - 1 \right) H_v^0(T) \quad (9)$$

where $H_v^{int}(T)$: total integral enthalpy of water adsorbed on microparticles (J mol^{-1}); $H_v^0(T)$: Integral molar enthalpy of condensation of pure water (J mol^{-1}).

The diffusion pressure (ϕ) was calculated as described by Nunes and Rotstein (1991):

$$\phi = \mu_{ap} - \mu_a = RT \frac{W_{ap}}{W_v} \int_0^{a_w} X_{eq} d \ln(a_w) \quad (10)$$

$$\phi = \alpha T \int_0^{a_w} X_{eq} d \ln(a_w) \quad (11)$$

$$\alpha = R \frac{W_{ap}}{W_v} \quad (12)$$

where ϕ : diffusion pressure or surface potential (J mol^{-1}); μ_{ap} : chemical potential of the pure adsorbent; μ_a : chemical potential of the adsorbent in the condensed phase; W_{ap} : molecular mass of the adsorbent; W_v : molecular mass of the water.

The value of α cannot be determined due to W_{ap} being unknown. But α is a constant and a process at constant ϕ/α is the same as a process at constant ϕ .

The values obtained for the ΔH_{int} were used for the calculation of the variation of integral molar entropy (ΔS_{int}) by Eq. (13), similar to the calculation of ΔS_{dif} :

$$(\Delta S_{int})_T = S_S - S_L = \frac{-(\Delta H_{int})_T - RT \ln(a_w)}{T} \quad (13)$$

where $S_S = S/N_1$: integral molar entropy of water adsorbed on the microparticles ($\text{J mol}^{-1} \text{K}^{-1}$); S : integral entropy of water adsorbed on microparticles ($\text{J mol}^{-1} \text{K}^{-1}$); S_L : molar entropy of condensation of pure water ($\text{J mol}^{-1} \text{K}^{-1}$).

2.4. Isokinetic compensation theory

The isokinetic compensation theory or enthalpy–entropy compensation proposes a linear relationship between the entropy and enthalpy of adsorption or desorption of water (Beristain et al., 1996), as shown in Eq. (14):

$$(\Delta H_{int})_T = T_B (\Delta S_{int})_T + \Delta G_B \quad (14)$$

In which T_B : isokinetic temperature (K); ΔG_B : Gibbs free energy associated with the isokinetic temperature (J mol^{-1}).

The verification of the theory of compensation can be performed by comparing the isokinetic temperature (T_B) with the harmonic mean temperature (T_{hm}) (Krug et al., 1976):

$$T_{hm} = \frac{n}{\sum_{i=1}^n \left(\frac{1}{T_i}\right)} \quad (15)$$

In which T_{hm} : harmonic mean temperature (K); n : number of temperatures used.

The confidence interval, $(1 - \alpha)$ 100%, for the isokinetic temperature (T_B) is given by:

$$T_B = \hat{T}_B \pm t_{m-2, \alpha/2} \sqrt{\text{Var}(T_B)} \quad (16)$$

$$\hat{T}_B = \frac{\sum [(H_{int})_T - (\overline{\Delta H_{int}})_T] [(\Delta S_{int})_T - (\overline{\Delta S_{int}})_T]}{\sum [(\Delta S_{int})_T - (\overline{\Delta S_{int}})_T]^2} \quad (17)$$

$$\text{Var}(T_B) = \frac{\sum [(\Delta H_{int})_T - \Delta G_B - \hat{T}_B \Delta S_{int}]^2}{(m-2) \sum [(\Delta S_{int})_T - (\overline{\Delta S_{int}})_T]^2} \quad (18)$$

In which T_B : slope inclination of the enthalpy–entropy compensation with a confidence interval of 95% calculated for all data sets; m : number of data pairs (ΔH_{int} , ΔS_{int}); $\overline{\Delta H_{int}}$: mean integral enthalpy; $\overline{\Delta S_{int}}$: mean integral entropy; $\text{Var}(T_B)$: standard error of the isokinetic temperature.

3. Results and discussion

3.1. Water vapor adsorption kinetics

The influence of temperature on the adsorption phenomenon for a relative humidity of 43.2%, Fig. 1a, and the influence of relative humidity at 25 °C, Fig. 1b, were evaluated. In the two kinetic curves it can be seen that from 144 h, the microparticles showed no change in mass over time, that is, they reached the water adsorption phenomenon equilibrium.

It was observed that with an increase in temperature from 15 °C to 45 °C, the water content adsorbed during the evaluated time decreased. Initially, in the formation of the first layer of adsorbed molecules, the temperature does not have great influence on the adsorption process, but with the formation of subsequent layers, the interaction forces between the adsorbent (matrix) and adsorbate (water molecules) decreases and since at higher temperatures the molecular agitation is higher due to the higher energy state, there is, thus, a reduction in the quantity of molecules adsorbed, resulting in lower adsorptive capacity.

Increasing the relative humidity from 11.3% to 84.3% for a temperature fixed at 25 °C, there was an increase in the adsorptive capacity of the microparticles because there is more adsorbate available, i.e., ambient air is saturated with adsorbate, however, this relationship has an end when the formation of the maximum possible number of layers of adsorbed molecules occurs, from this point on, the whole water gain in the system is associated with an absorption process, because gum arabic is a complex polysaccharide with a highly branched structure containing shorter chains and more hydrophilic groups, which favors the absorption of water.

The adsorption kinetics data for powdered food products are scarce in the literature. The behavior of a kinetic curve similar to that of rosemary essential oil microparticles was observed for powdered whole milk (Szulc and Lenart, 2012).

3.2. Monolayer moisture content (X_m)

The values of X_m (Fig. 2) were estimated by fitting the GAB model (Eq. (1)) to the experimental data of water adsorption. The moisture content of the monolayer decreases with increasing

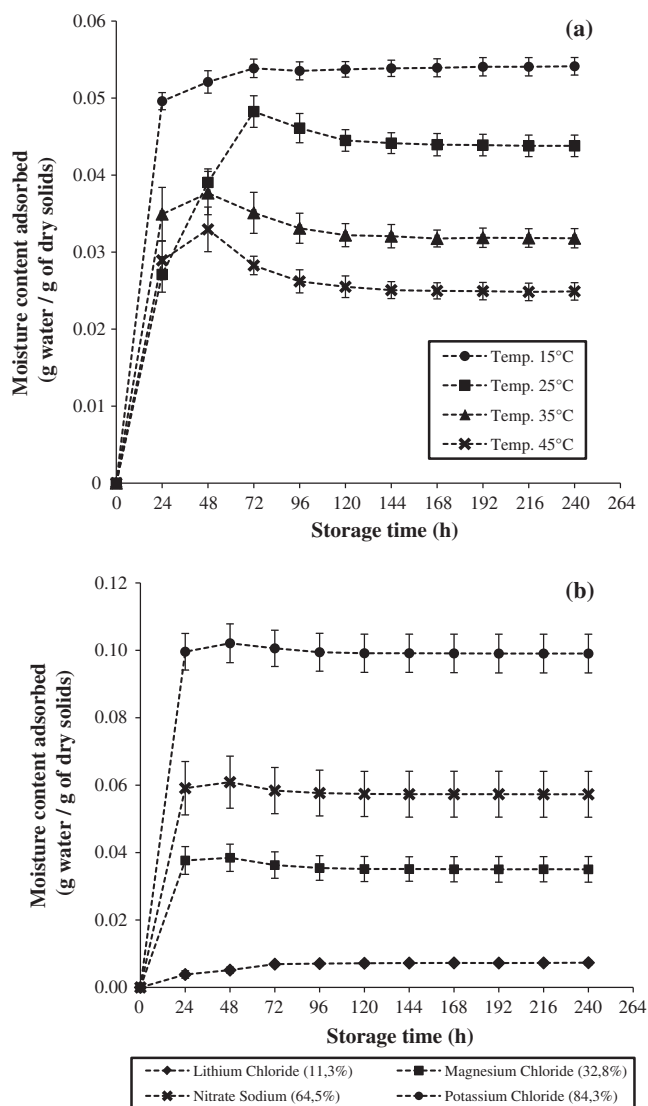


Fig. 1. Adsorption kinetics of rosemary essential oil microparticles: (a) influence of temperature (RH = 43.2%); (b) influence of relative humidity at 25 °C.

temperature. The relationship between the X_m of the microparticles and the temperature was expressed by Eq. (19):

$$X_m = -0.132t + 14.63 \quad (19)$$

In which t is the temperature in °C and the coefficient of determination (R^2) was 0.973.

Rizvi (1986) conducted a data survey in the literature concerning the effect of temperature on various dehydrated products and noted that X_m decreases with increasing temperature. This behavior was attributed to a reduction in the number of active sites due to physical and chemical changes induced by temperature.

3.3. Gibbs free energy

The Gibbs free energy, a quantitative measure of the affinity between water molecules and the surface of the microparticle, indicates the energy required for a molecule in the vapor state to pass to the adsorbed state and also the degree of spontaneity of the adsorption process (Bhattacharya et al., 2008; Dotto et al., 2013; Ren et al., 2013). Fig. 3 shows the Gibbs free energy (ΔG) according to the X_{eq} for the temperatures evaluated from 15 °C to 45 °C, calculated by means of Eq. (2).

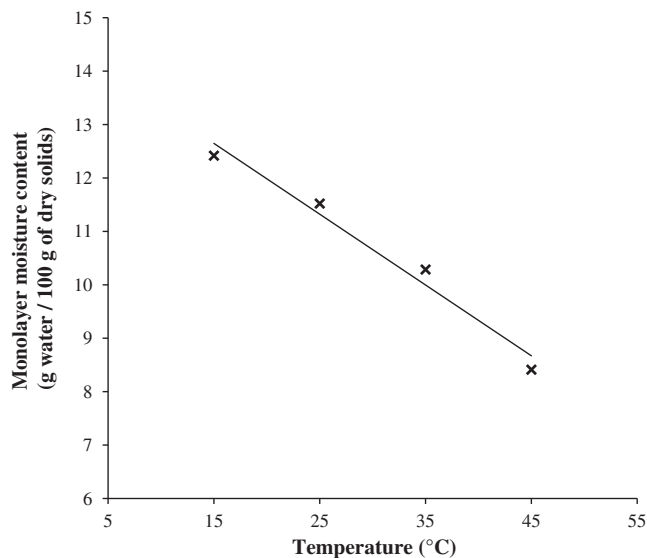


Fig. 2. Variation of the monolayer moisture content of rosemary essential oil microparticles with temperature.

The ΔG values continuously increase with increasing X_{eq} values and tend toward a constant value close to zero. For the whole X_{eq} range and all temperatures, the ΔG was negative, indicating that the adsorption phenomenon is a spontaneous process. The more negative the ΔG , values, the more spontaneous and energetically favorable is the adsorption process (Bhattacharya et al., 2008). At high X_{eq} levels, adsorption occurs with less spontaneity, since under this condition the formation of water molecule multilayers certainly occurred and the interaction forces between the matrix and the adsorbate were reduced.

Results similar to the ΔG behavior, as a function of X_{eq} , have been reported for other microparticles obtained by spray-drying (Bonilla et al., 2010; Viganó et al., 2012) and durum semolina wheat (Oulahna et al., 2012).

3.4. Differential and integral enthalpy

The net differential enthalpy ($-\Delta H_{dif}$) and the net integral enthalpy ($-\Delta H_{int}$) as a function of X_{eq} at the temperature of 25 °C are presented in Fig. 4. The microparticles showed negative ΔH_{int} for the entire range of moisture and temperature considered and ΔH_{dif} showed positive values for moisture content of 7–8.25 g water/100 g dry solids and from this range on, were negative.

Initially, at low moisture content, it was observed a continuous increase of both net enthalpy values up to a maximum value in $-\Delta H_{dif}$ and $-\Delta H_{int}$, that correspond to $-11166.3 \text{ J mol}^{-1}$, for X_{eq} corresponding to 11.97 g of water/100 g dry solids, for ΔH_{dif} , and $-16221.9 \text{ J mol}^{-1}$, for X_{eq} corresponding to 10.4 g of water/100 g dry solids for ΔH_{int} . After the maximum values, there is a reduction in the net enthalpy values with the increase of X_{eq} . Behavior similar to that of $-\Delta H_{dif}$ and $-\Delta H_{int}$ in function of X_{eq} has been reported for other microparticles obtained by spray drying, such as allspice essential oil encapsulated with a mixture of whey protein isolate, mesquite gum and maltodextrin (Sánchez-Sáenz et al., 2011), canola oil encapsulated with mesquite gum (Bonilla et al., 2010), peppermint oil encapsulated with maltodextrin (Adamiec, 2009) and pure gum arabic (Pérez-Alonso et al., 2006).

The authors explained that negative enthalpy confirms the existence of strong attractive interactions between the surface of the microparticle and water and that the initial increase in net enthalpy with the increased moisture content may be associated

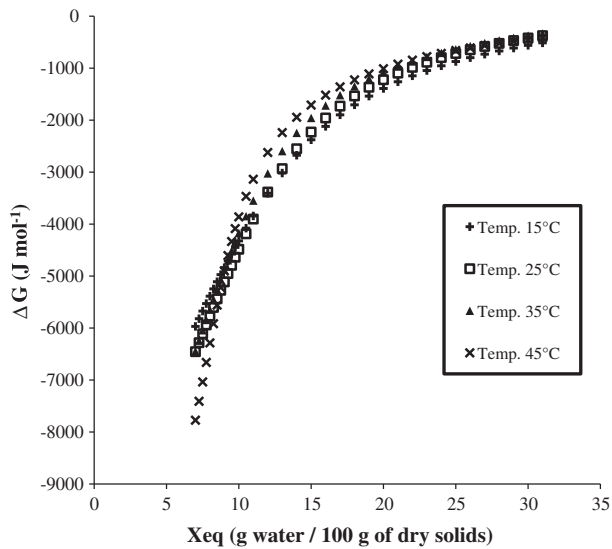


Fig. 3. Changes in Gibbs free energy as a function of moisture content for the rosemary essential oil microparticles.

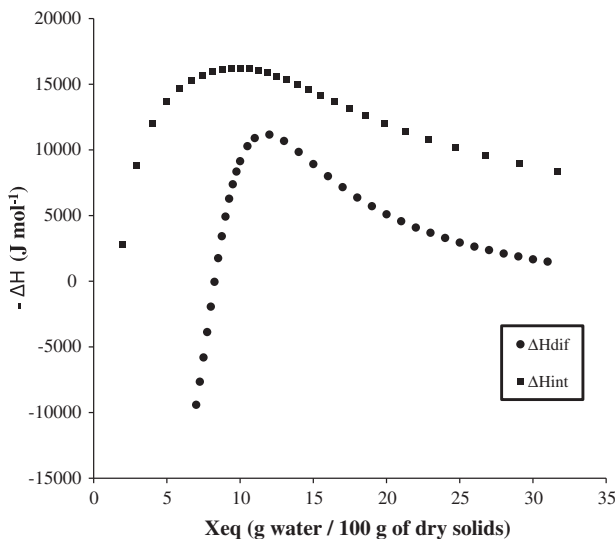


Fig. 4. Differential and integral enthalpy changes for water sorption on microparticles of rosemary essential oil at 25 °C.

with swelling of the polymer matrix, gum arabic, due to the increase in moisture content. This swelling causes new high energy adsorption sites to be exposed, where other water molecules can be adsorbed. They concluded that the maximum enthalpy value indicates the covering of larger and more energetic binding sites and that the decrease of the enthalpy values, after the peak, indicates that fewer active sites are available for adsorption, which initiates the multilayer formation.

The ΔH_{int} for the microparticles was higher, in modulus, than the ΔH_{dif} for the entire moisture range. This result is consistent with the definition of these quantities, since ΔH_{dif} represents the energy needed for water molecules to bind (adsorb) on a given surface at a given moisture content, while ΔH_{int} represents the mean energy of all the molecules bound (adsorbed) to the surface (Schneider, 1981).

According to Liebanes et al. (2006) using the total differential enthalpy (H_v^{dif}) to determine the strength or intensity of the bond between water and the food surface is questioned by some

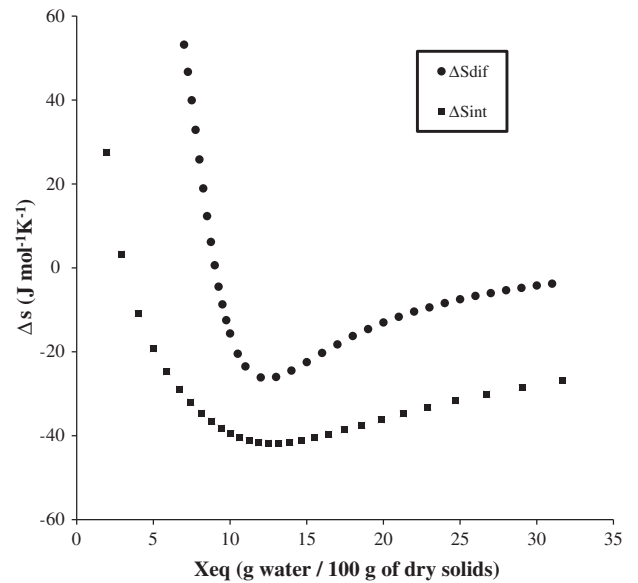


Fig. 5. Changes in the differential and integral entropies as a function of moisture content at 25 °C for the microparticles of rosemary essential.

researchers because of its differential nature. Hill (1949) stated that the actual adsorption enthalpy, that represents the equilibrium of the adsorbed molecules, is given in terms of the total integral enthalpy (H_v^{int}) of adsorbed water at a constant diffusion pressure (ϕ). The H_v^{int} represents the total energy required to remove water from the food surface. This parameter provides an indication of the bond intensity of water molecules with the food or food material surface, which may be used in the energy drying equilibrium and freezing operations (Gal, 1975).

The value of X_{eq} corresponding to the maximum net integral enthalpy ($-\Delta H_{int}$) was close to the value found for the monolayer moisture content (X_m), estimated by the GAB model (Table 1). For the temperatures of 15 °C, 25 °C, 35 °C and 45 °C there were, respectively, 11.380, 10.043, 8.767, 7.327 g of water/100 g dry solids. A similar result was reported by Kaya and Kahyaoglu (2007). This result is consistent, because X_m indicates the amount of water that is strongly adsorbed at specific sites and to break these bonds maximum energy is required compared to other moisture contents.

3.5. Differential and integral entropy and maximum stability conditions

Fig. 5 presents the variation of differential entropy (ΔS_{dif}) and integral entropy (ΔS_{int}) as a function of X_{eq} at 25 °C. The ΔS_{dif} and ΔS_{int} magnitudes were negative for the entire range of X_{eq} and these negative values are attributed to the existence of chemical adsorption and/or changes in the structure of the adsorbent (Iglesias et al., 1976).

The microparticles showed a decrease of ΔS_{dif} and ΔS_{int} the increase of moisture to a minimum of $-20.936 \text{ J mol}^{-1} \text{ K}^{-1}$ and $-41.868 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively, and then an increase in magnitude with the increase of X_{eq} . The minimum points for both entropies are possibly caused by the attachment of water molecules, resulting in their loss of rotational freedom and randomness due to the strong bond with the adsorbent matrix (McMinn and Magee, 2003). The minimum entropy can occur when there are strong interactions between the adsorbate and adsorbent, and thus, the water becomes less available to participate in deterioration reactions (Nunes and Rotstein, 1991).

Similar results to the behavior of ΔS_{dif} and ΔS_{int} in function of X_{eq} have been reported for various microparticles obtained by spray drying, such as orange oil encapsulated with mesquite gum (Beristain et al., 2002), among others (Bonilla et al., 2010; Sánchez-Sáenz et al., 2011).

ΔS_{int} is the parameter that is directly related to the stability of the rosemary essential oil microparticles, because it indicates the degree of order–disorder in a system, and the higher the disorder, the higher the entropy associated with the system (Rizvi and Benado, 1984).

The minimum values of ΔS_{int} are related to the water activity (a_w) in which a food product has the best stability, i.e., they can be used for the selection of appropriate storage conditions for a food or additive, so that its aroma, taste, color, texture, nutrient and microbiological stability undergo minimal changes (Bonilla et al., 2010; Domínguez et al., 2007; Nunes and Rotstein, 1991; Pérez-Alonso et al., 2006; Viganó et al., 2012). This minimum value occurs when the bond between the adsorbent and the adsorbate is very strong and therefore there is less water available for deterioration reactions, whether physical, chemical or microbiological (Nunes and Rotstein, 1991). Thus, under these conditions the product has increased shelf life.

The conditions for maximum microparticle stability were obtained from the analysis of ΔS_{int} and a_w and X_{eq} conditions related to the minimum point (Table 2). With increasing temperature there is a decrease in the a_w of the most stable region, which also significantly reduces the amount of moisture adsorbed on the product. Pérez-Alonso et al. (2006) studied the maximum stability conditions for powdered gum arabic obtained by spray drying and found that the highest stability occurred at values of 0.574, 0.386 and 0.316 in relation to temperatures over 25 °C, 35 °C and 40 °C, respectively, behavior similar to that found in this present work.

3.6. Enthalpy–entropy compensation

The theory of enthalpy–entropy compensation or isokinetic compensation theory, proposes a linear relationship between the enthalpy and differential entropy in a given process and is used to evaluate the adsorption and desorption of water. It is a useful tool to clarify the information about the mechanisms that control the sorption of water vapor in food (Azura and Beristain, 2006; Beristain et al., 1996). The theory only applies if the isokinetic temperature (T_B) is different from the harmonic mean temperature (T_{hm}) (Krug et al., 1976). The T_{hm} was calculated by Eq. (15) and was obtained at a temperature of 302.74 K.

The isokinetic temperatures were calculated using Eq. (14) and the confidence interval of 95% was calculated using Eqs. (16)–(18). The enthalpy–entropy compensation approach, applied to the rosemary essential oil microparticles for the integral thermodynamic properties at 25 °C (Fig. 6), resulted in two compensation lines (represented by arrows) that indicate adsorption regions, related to low and intermediate-high water activity values. The arrowheads indicate the direction of adsorption from lowest to highest moisture equilibrium.

Each of the arrows indicates the existence of an isokinetic temperature. The temperatures are represented in the following ways: T_{B1}^{int} (integral isokinetic temperature associated with low a_w values)

Table 2
Maximum stability conditions of rosemary essential oil microparticles.

Temperature (°C)	a_w	X_{eq} (g water 100 g ⁻¹ dry powder)	R^2
15	0.358	14.715	0.998
25	0.292	12.713	0.998
35	0.250	10.998	0.998
45	0.119	8.447	0.997

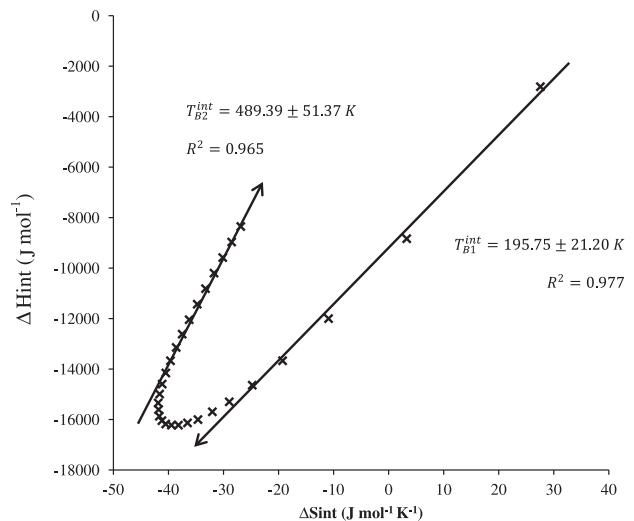


Fig. 6. Enthalpy–entropy relationship for water sorption on of rosemary essential oil microparticles at 25 °C.

and T_{B2}^{int} (integral isokinetic temperature associated with intermediate-high a_w values). The isokinetic temperatures (T_{B1}^{int} , T_{B2}^{int}) differed from T_{hm} and thus, the adequacy of isokinetic compensation for the water vapor adsorption on the microparticles was confirmed.

If the $T_B > T_{hm}$, the process is driven by enthalpy, whereas if $T_B < T_{hm}$, the process is controlled by entropy (Leffler, 1955). It was found that $T_{B1}^{int} < T_{hm}$ ($195.75 \pm 21.20 \text{ K} < 302.74 \text{ K}$) and $T_{B2}^{int} > T_{hm}$ ($489.39 \pm 51.37 \text{ K} > 302.74 \text{ K}$), thus for the low moisture content, the process was controlled by entropy, i.e., the barriers which limit the water molecules in the product microstructure are more important than the interaction energy related to the chemical composition of the microparticles, and in the intermediate-high moisture, the process was controlled by enthalpy, that is, the water vapor adsorption mechanisms are controlled by energy interactions related to the chemical composition of the product (Beristain et al., 1996). Importantly, at the point of lowest entropy, the process is not controlled by entropy nor enthalpy, as there is an equilibrium between both mechanisms (Viganó et al., 2012), i.e., the values near minimum entropy are not considered for the T_B calculation.

Similar results where the enthalpy–entropy compensation approach resulted in two lines of compensation have been reported in the adsorption of water in starchy materials (Beristain et al., 1996), pineapple pulp powder obtained by spray drying (Viganó et al., 2012) and microparticles of canola oil, which, when using soy protein isolate as encapsulant, an isokinetic temperature related to the low a_w range of $99.84 \pm 16.21 \text{ K}$ and for the high a_w range, an isokinetic temperature of $556.96 \pm 193.99 \text{ K}$ (Bonilla et al., 2010).

4. Conclusion

The adsorption of water on rosemary essential oil microparticles is a spontaneous phenomenon and the time required to reach equilibrium between the phases does not depend on the temperature or moisture under which the product is stored. The GAB equation was helpful for the representation of the microparticle adsorption behavior, thermodynamic properties calculations and predicting ideal storage conditions.

The thermodynamic analysis has provided important information about the mechanisms that control the sorption of water vapor on the powdered product. The minimum values for the net

integral entropy were indicative of maximum stability conditions of the product, corresponding to water activities of 0.358–0.119, in the temperature range from 15 °C to 45 °C, respectively. Isokinetic compensation was confirmed for the adsorption phenomenon of the microparticles and the approach resulted in two compensation lines. At a low moisture content the process was controlled by entropy, that is, the barriers which limit the water molecules within the product microstructure are more important than the interaction energy related to the chemical composition of the microparticles, and with the intermediate-high moisture content, the process was controlled by enthalpy.

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