

Establishing the Most Suitable Storage Conditions for Microencapsulated Allspice Essential Oil Entrapped in Blended Biopolymers Matrices

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The adsorption isotherms of allspice essential oil microencapsulated in biopolymers blend (whey protein concentrate [WPC], mesquite gum [MG], and maltodextrin DE10 [MD]) in different proportions (WPC17%-MG17%-MD66% w/w and WPC66%-MG17%-MD17% w/w) with wall-to-core material ratios of 4:1 were determined at 25, 35, and 40°C. The isotherms were fitted using the Guggenheim-Anderson-de Boer (GAB) model and the enthalpies and entropies, both differential and integral, were estimated by the Clausius-Clapeyron method. The minimum integral entropy was considered as the point of maximum stability where strong bonds between the adsorbate and adsorbent occurred, and water would be less available and likely to participate in spoilage reactions. The point of maximum stability was found between 13.79 and 15.11 kg H₂O/100 kg d.s. (corresponding to water activity, a_w , of 0.444–0.551) for the microcapsules with WPC17%-MG17%-MD66% w/w as wall material and 18.71–19.63 kg H₂O/100 kg d.s. (a_w =0.591–0.713) for the microcapsules with WPC66%-MG17%-MD17% w/w as wall material in the temperature range studied.

Keywords Adsorption isotherms; Biopolymers blends; Differential and integral enthalpies and entropies; Microencapsulated allspice essential oil

INTRODUCTION

Most liquid food flavorings are volatile and chemically unstable in the presence of air, light, moisture, and high temperatures, including allspice (*Pimenta dioica* L. Merril) essential oil. Jamaica is the largest producer and exporter of pimento, accounting for 70% of the world trade. The

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remaining 30% is produced by Mexico, Guatemala, Honduras, Belize, and Brazil.^[1] The allspice essential oil is incorporated in processed foods and in patent drugs to add both flavor and aroma, whereas in the cosmetic industry it finds its ways into many exotic perfumes, cosmetics, soaps, and aftershaves.^[2,3]

Spray-drying microencapsulation is widely employed for the preparation of dry stable additives, essential oils, and flavors and involves the emulsification of a core material, usually a lipid, with a dense solution of wall material such as a protein, vegetable gum, maltodextrin, or modified starch and atomization and drying of the emulsion.^[4] In order to obtain efficient microcapsules, these biopolymers must possess excellent emulsification properties and form semipermeable membranes that limit oxygen transfer, because oxidation is considered a preponderant factor in determining the shelf life of most core materials.^[5] Suitable wall materials for retarding lipid oxidation are those in which the drying rate decreases rapidly as water content is decreased and form fine, dense networks as soon as the drying commences (type 1 curves).^[5–7] However, not all of the biopolymers showing type 1 curves are good emulsifiers and are not suitable for lipid encapsulation when used alone. Thus, it is desirable to determine an optimal combination of materials that will produce a synergistic effect, providing excellent emulsifying capacity and oxygen barrier properties. A reliable method for selecting a priori suitable biopolymer blends for protecting microencapsulated lipids against oxidation are those showing type 1 isothermal drying behavior and exhibiting relatively higher activation energies.^[6,7]

Another important aspect of microcapsules is to determine the most suitable storage conditions guaranteeing long-term microbiological, physical, and chemical

stability.^[8] The thermodynamics of water vapor sorption provide a reliable criterion for predicting the storage stability and shelf life of dehydrated food products.^[8] Thermodynamic functions for analysis of sorption behavior include enthalpy and entropy, both differential and integral, and Gibbs free energy.^[8] Thermodynamic analysis of sorption requires knowledge of isotherm behavior as a function of temperature. The Guggenheim-Anderson-de Boer (GAB) equation is a localized multilayer sorption and condensed film model. It is widely regarded as the best theoretical model for sorption phenomena in foods, because it provides valuable information on the changes related to the sorption energy of the system.^[9] The free energy required for transferring a water molecule from the vapor state to the adsorbed state is a quantitative measure of the affinity between the dry food-water and indicates the degree of spontaneity of the adsorption process.^[10] Differential enthalpy of sorption is a differential molar quantity derived from the temperature dependence of the isotherm, and it represents the energies for water molecules binding at a particular hydration level, whereas the integral enthalpy is the average energy of all molecules already bound at that level.^[8,11] The differential and integral entropies are obtained from the differential and integral enthalpies, respectively. The minimum integral entropy pinpoints the water activity at which a dry food product is most stable^[12] and where strong bonds between the water (adsorbate) and the food (adsorbent) occur.^[13] Variations in biopolymer matrices will interact differently with water and thus require different storage conditions (water activity and temperature) to achieve optimal stability.

The objective of this work was to (1) microencapsulate allspice essential oil in two biopolymer blends (whey protein concentrate, mesquite gum, and maltodextrin DE10, in different proportions); (2) evaluate the water adsorption process of the microcapsules of allspice essential oil using differential and integral thermodynamic properties; and (3) calculate the minimum integral entropy as a criterion for predicting the water activity and temperature, providing the most suitable storage conditions for the allspice essential oil microcapsules.

MATERIALS AND METHODS

Materials

Whey protein concentrate (WPC) with 80% protein on dry basis was purchased from Hilmar Ingredients (HilmarTM 8000, Hilmar, CA). Mesquite gum (MG)^[14] was hand collected in the form of teardrops from *Prosopis laevigata* trees in the Mexican State of San Luis Potosí and purified as indicated by Vernon-Carter et al.^[15] Maltodextrin DE10 (MD) was obtained from Complementos Alimenticios S.A. de C.V. (MaltadexTM 10, Naucalpan, Mexico).

Allspice (*Pimenta dioica* L. Merrill) fruits were purchased from a plantation in the Mexican State of Veracruz, Mexico.

The allspice essential oil (AEO) was obtained by hydrodistilling 1 kg of dried and crushed allspice fruits with 4 L of bidistilled water in a multifunctional solid-liquid batch extractor-reactor (Pignat model UPR-1000, Genas, France), at 92°C and using four extraction stages (30 min per stage). The volatilized oil carried by the steam was condensed, decanted, and purified with methylene chloride (15:100 ratio) by simple distillation in a rotatory evaporator (Yamato, model RE500, Tokyo, Japan).^[16] Composition of AEO was determined by gas chromatography (Agilent 6890, model G1530A, Santa Clara, CA) equipped with an autosampler (model 7683B), a flame ionization detector (FID), and a CP-Sil 88 column (100 m × 0.25 mm × 0.39 mm). Initial column temperature was 50°C, and a heating ramp of 4°C/min was used until 310°C was achieved. N₂ was used as carrier gas at a flow rate of 1.0 mL/min. AEO was made up of 24 compounds, with methyl eugenol, eugenol, and myrcene accounting for 48.7, 16.3, and 17.1% of AEO and the rest of the compounds in concentrations lower than 6.1%. This composition was very similar to that reported by Krishnamoorthy and Rema.^[1]

Preparation of the Oil-in-Water Emulsions

WPC, MG, and MD were solubilized in water in two different proportions: WPC17%-MG17%-MD66% w/w and WPC66%-MG17%-MD17% w/w. It has been reported that both blends had good emulsifying properties, so the use of an emulsifier is not required, but that the former blend provided better thermooxidative stability to microencapsulated chili oleoresin than the latter.^[17] The required amount of AEO was added dropwise to the two biopolymer blends to obtain oil-in-water emulsions ($E_{\text{WPC17\%-MG17\%-MD66\%}}$ and $E_{\text{WPC66\%-MG17\%-MD17\%}}$) with a dispersed-phase volume fraction (ϕ) of 0.10 and a total biopolymers solids-to-AEO ratio of ratio of 4:1. Emulsification was carried out with an Ultra-Turrax T50 homogenizer (IKA[®]-WERKE Works Inc., Wilmington, NC) at a speed of 5,800 rpm for 6 min. The biopolymer solutions were maintained in an ice-water bath in order to keep the emulsion temperature below 30°C.

Microcapsule Formation

$E_{\text{WPC17\%-MG17\%-MD66\%}}$ and $E_{\text{WPC66\%-MG17\%-MD17\%}}$ were spray-dried in a Büchi model 190 spray dryer (Büchi Laboratories Technik AG, Flawil, Switzerland) using an inlet air temperature of 170 ± 5°C, an outlet air temperature of 95 ± 5°C, an atomization pressure of 4.5 bar, and flow rate of 20 mL/min; microcapsules of $M_{\text{WPC17\%-MG17\%-MD66\%}}$ and $M_{\text{WPC66\%-MG17\%-MD17\%}}$ were obtained.

Emulsion and Microcapsule Particle Size

The volume fraction-length mean size ($d_{4,3}$) of microcapsules and of the emulsions from which they were

obtained were determined with a Mastersizer 2000 (Malvern Instruments, Ltd., Malvern, Worcestershire, England). Emulsions were dispersed in water and microcapsules in propan-2-ol. Additionally, the span of the oil-in-water emulsions, a dimensionless width parameter that can provide a relative measure the polydispersity of the emulsion's droplet size,^[18] was determined.

Encapsulation Efficiency

Given the wide array of compounds making up the allspice essential oil, we decided to use eugenol as the target compound to determine the allspice essential oil encapsulation efficiency in the microcapsules. The total and surface eugenol content of microcapsules was determined using the methodology described by Beristain et al.^[19] with slight variations. Total oil in the powders was determined using a Clevenger hydrodistillation apparatus (Hamabala Cantt, Haryana, India). Ten grams of powder was dissolved in 150 mL distilled water in a 250-mL flask. A few boiling spheres and ca. 0.5 mL antifoam (silicon oil, Aldrich, Toluca, Mexico) were added. A Clevenger oil trap and water cool condenser were attached. The solution was slowly brought to a boil and allowed to distill for 3 h, gathering the oil in the collection arm. Surface oil was determined gravimetrically. Ten grams of powder was placed in an extraction thimble and covered with glass wool. The powder was extracted with hexane for 4 h. Each extract was evaporated to dryness in a water bath at 30°C and completely dried in a vacuum oven at 60°C. Eugenol contents in total and surface oil were determined spectrophotometrically by measuring the oil absorbance at 283 nm using the methodology described by Fagen et al.^[20] The encapsulation efficiency (EE) of eugenol was determined from the experimental data obtained at $t = 0$ with the following equation:^[21]

$$EE = [(total E_M - surface E_M)/total E_M] \times 100 \quad (1)$$

Sorption Isotherms

The $M_{WPC17\%-MG17\%-MD66\%}$ and $M_{WPC66\%-MG17\%-MD17\%}$ powders were put into glass Petri dishes, taking care that the powders completely and homogeneously covered the dishes surface.^[22] The dishes were then introduced into glass desiccators containing P_2O_5 as a desiccant at room temperature ($18 \pm 2^\circ C$) for 3 weeks in order to reduce to a minimum relative humidity ($\sim 2\%$) of the powders. The adsorption isotherms were determined by the gravimetric method described by Lang et al.^[23] Approximately 1.0 ± 0.1 mg samples of $M_{WPC17\%-MG17\%-MD66\%}$ and $M_{WPC66\%-MG17\%-MD17\%}$ were put into small glass desiccators of 10 cm diameter that contained saturated solutions of different salts that provided water activities (a_w) in the range of 0.11–0.85.^[24] Filter paper (Whatman No. 1) was placed above the saturated salt solutions, in a

perforated plate used as support for the powders to allow moisture transmission. Five desiccators with each powder were placed into a forced convection drying oven (Riossa, model E-51, Mexico City, Mexico) at 25, 35, and 40 (± 0.1)°C. The powders were weighed with an Ohaus electronic balance (model AP210, Pine Brook, NJ) every 5 days until equilibrium was achieved. Equilibrium was assumed when the difference between two consecutive weightings was less than 1 mg/g of solids. The time to reach equilibrium varied from 20 to 25 days. Moisture content of the humidified systems was determined by difference in weight after drying in a vacuum oven (FELISA, Mexico City, Mexico) at 60°C in the presence of magnesium perchlorate desiccant. The water activity was measured with an Aqualab water activity meter with temperature compensation (model series 3 TE, Decagon Devices, Inc., Pullman, WA). Longer drying times did not produce a sample weight decrease of more than 0.1 mg.

The GAB equation is mathematically expressed as:^[25]

$$M = \frac{M_0 CKa_w}{(1 - Ka_w)(1 - Ka_w + CKa_w)} \quad (2)$$

where C and K are constants related to the energies of interaction between the first and distant sorbed molecules at the individual sorption sites. Theoretically they are related to sorption enthalpies as follows:

$$C = c' \exp \frac{(h_m - h_n)}{RT} \quad (3)$$

$$K = k' \exp \frac{(h_1 - h_m)}{RT} \quad (4)$$

The parameters were estimated by fitting the mathematical model to the experimental data, using nonlinear regression with Origin version 8.5 Scientific Graphing and Analysis Software (OriginLab Corp., Northampton, MA).

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 Eq. (5).^[26–28] It is generally assumed that a good fit is obtained when $E < 5\%$.

$$E = \frac{100}{n} \sum \frac{|M_i - M_{Ei}|}{M_i} \quad (5)$$

Thermodynamic Properties

The free energy for water adsorption was calculated using Gibbs' equation:

$$\Delta G = RT \ln a_w \quad (6)$$

Differential Properties

The differential enthalpy change is obtained from equilibrium sorption data, representing the difference between the latent heat of adsorption and the latent heat of condensation of pure water. It can be determined from the following equation, which is derived from the Clausius-Clapeyron equation:^[25]

$$\left(\frac{\partial \ln(p/p_0)}{\partial(1/T)}\right)_M = \left(\frac{\partial \ln a_W}{\partial(1/T)}\right)_M = \frac{h_l - H_l}{R} = \frac{\Delta H_{dif}}{R} = \frac{q_{st}}{R} \quad (7)$$

The differential enthalpy of sorption is nearly equal to the isosteric heat of sorption (q_{st}):^[29]

$$\Delta H_{dif} = q_{st} - RT \quad (8)$$

The use of the Clausius-Clapeyron equation implies that the moisture content of the system under consideration remains constant and that the enthalpy of vaporization of pure water (as well as the excess heat of sorption) does not change with temperature.^[25]

The change in molar differential entropy of adsorption can be calculated from the Gibbs-Helmholtz equation, as used by Beristain et al.:^[30]

$$\Delta S_{dif} = s_l - S_l = \frac{\Delta H_{dif}}{T} - R \ln a_W \quad (9)$$

Integral Properties

The integral molar enthalpy can be calculated using an equation similar to Eq. (6) but maintaining constant the diffusion pressure, Φ , constant.^[13]

$$\left(\frac{\partial \ln(p/p_0)}{\partial T}\right)_\Phi = \frac{H_g - H_s}{RT^2} \quad (10)$$

Rearranging Eq. (10) and taking pure water as the reference state at temperature T :

$$\left(\frac{\partial \ln a_W}{\partial(1/T)}\right)_\Phi = \frac{H_s - H_l}{R} = \frac{\Delta H_{int}}{R} \quad (11)$$

$$\Phi = \mu_{ap} - \mu_a = RT \frac{W_{ap}}{W_v} \int_0^{a_W} M d \ln a_W \quad (12)$$

$$\Phi = \alpha_1 T \int_0^{a_W} M d \ln a_W \quad (13)$$

Changes in molar integral entropy can be calculated using Eq. (14):^[31]

$$(\Delta S_{int})_T = S_s - S_l = \frac{(\Delta H_{int})_T}{T} - R \ln a_W \quad (14)$$

Statistical Analyses

Analysis of variance (ANOVA) and Tukey's test ($p \leq 0.05$) were performed on particle size and eugenol content results using the software NCSS 2000 (Wireframe Graphics, Kaysville, UT). All experiments were done in triplicate.

RESULTS AND DISCUSSION

E_{WPC66%-MG17%-MD17%} had a significantly smaller $d_{4,3}$ and span than E_{WPC17%-MG17%-MD66%} (Table 1). This result was expected because in the former emulsion the combined proportion of WPC and MG, which are considered very good emulsifiers,^[32,33] was overwhelmingly larger than that of MD, known for its almost devoid emulsifying capacity,^[34] whereas in the latter emulsion, MD is the dominating biopolymer in the blend. However, M_{WPC66%-MG17%-MD17%} and M_{WPC17%-MG17%-MD66%} showed nonsignificant differences in mean particle size, although both microcapsules exhibited significantly higher $d_{4,3}$ than their emulsion counterparts. When transforming

TABLE 1
Physicochemical properties of allspice essential oil-in-water emulsions and microcapsules

	Oil-in-water emulsion		Powder microcapsules		
	$d_{4,3}$ (μm)	Span	Moisture (kg water/ 100 kg dry solids)	$d_{4,3}$ (μm)	EE (kg eugenol retained/ 100 kg eugenol used in microcapsules formulation)
WPC17%-MG17%- MD66%	3.32 ± 0.01^b	1.402 ± 0.009^b	4.73 ± 0.17^a	9.60 ± 0.14^a	86.21 ± 3.22^b
WPC66%-MG17%- MD17%	1.81 ± 0.03^a	1.156 ± 0.005^a	5.38 ± 0.28^b	9.46 ± 0.19^a	76.49 ± 2.57^a

Values in the same column with different superscripts are significantly different ($p < 0.05$). M = microcapsule, WPC = whey protein concentrate, MG = mesquite gum, MD = maltodextrin DE 10.

an emulsion into a powder, a driving force of dissolved gases from the feed during the drying will occur as water is evaporated and as the droplet temperature increases, lowering the solubility of air.^[35,36] The entrapped gases tend to escape and diffuse through the biopolymeric matrix, and the greater the resistance opposed by the matrix to the gas diffusion, the larger the resulting microcapsule. Thus, it may be assumed that the biopolymeric matrix of $M_{WPC17\%-MG17\%-MD66\%}$ offered less resistance to gas diffusion than that of $M_{WPC66\%-MG17\%-MD17\%}$, probably because MD forms less viscous solutions than MG and WPC.

The encapsulation efficiency of eugenol was significantly higher in $M_{WPC17\%-MG17\%-MD66\%}$ than in $M_{WPC66\%-MG17\%-MD17\%}$; therefore, it may be inferred that the porosity of the former microcapsule was less than that of the latter microcapsule. These results seem to be

confirmed by the moisture content of the microcapsules, which was significantly higher in $M_{WPC66\%-MG17\%-MD17\%}$ than in $M_{WPC17\%-MG17\%-MD66\%}$.

The experimental sorption isotherms at 25, 35, and 40°C for $M_{WPC17\%-MG17\%-MD66\%}$ and $M_{WPC66\%-MG17\%-MD17\%}$ are shown in Figs. 1a and 1b, respectively. The adsorption isotherms of the microcapsules had a typical sigmoid shape,^[37] such as shown by apple pectin, soy protein, whey protein, sodium caseinate,^[38] defatted canola meal,^[39] powder of juice lemon with maltodextrin (MD-DE20) and gum arabic (GA),^[40] and a blend of MG, GA, and MD (17:66:17 ratio).^[41] Generally, the equilibrium moisture content is expected to decrease with increasing temperature at constant water activity.^[42] This trend was observed for $M_{WPC17\%-MG17\%-MD66\%}$ (Fig. 1a) but not for $M_{WPC66\%-MG17\%-MD17\%}$ (Fig. 1b), where moisture content increased with the temperature. This behavior has been observed in GA, microcrystalline cellulose, and fish protein myosin and has been attributed to a complex process not only involving adsorption but also structural changes (crystalline or amorphous) of the polymer matrix due to swelling and physical and/or chemical damage occurring during the spray-drying process.^[41-43] The relative position of the isotherms as a function of temperature and their shape is influenced by sample composition and the drying process conditions, because they affect the conformation and topology of the formulation components.

The experimental sorption isotherms data at 25, 35, and 40°C for both AEO microcapsules fitted very well with the GAB model. The GAB model parameters obtained are given in Table 2. The mean relative deviation modulus value was less than 5% at 25, 35, and 40°C and the coefficient of determination r^2 was over 0.994 for both samples. The value of the monolayer (M_0) fell within the range of

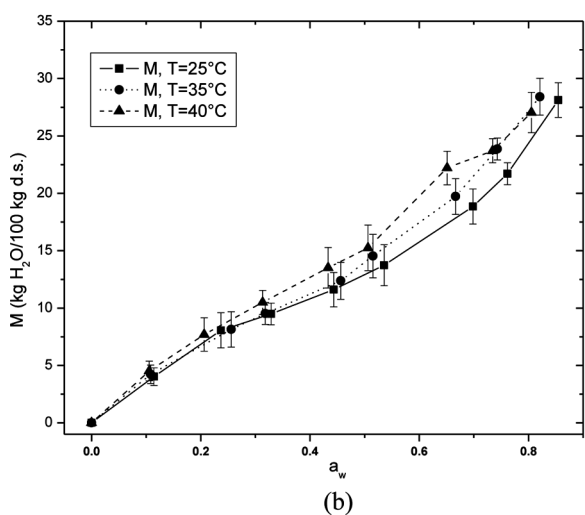
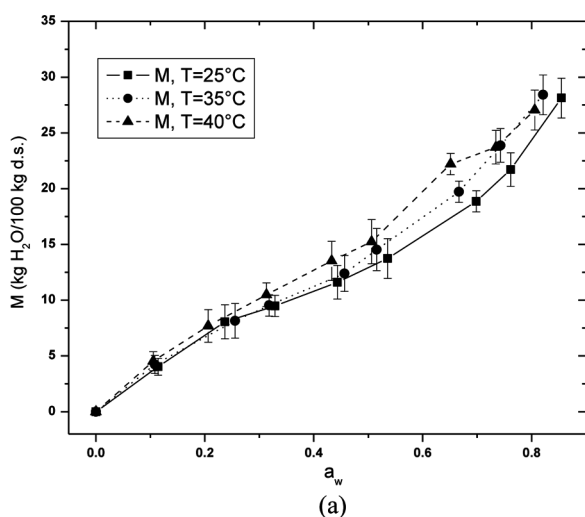


FIG. 1. Moisture sorption isotherms for (a) $M_{WPC17\%/MG17\%/MD66\%}$ and (b) $M_{WPC66\%/MG17\%/MD17\%}$.

TABLE 2

Estimated parameters of the GAB equation for microencapsulated allspice essential oil in biopolymer matrices of different proportions with wall-to-core material ratio of 4:1

T (°C)	M_0 (kg H ₂ O/ 100 kg d.s.)	C	K	r^2	E (%)
$M_{WPC17\%-MG17\%-MD66\%}$					
25	6.83	17.01	0.960	0.999	0.09
35	8.78	13.25	0.912	0.999	0.83
40	10.14	17.77	0.865	0.999	0.20
$M_{WPC66\%-MG17\%-MD17\%}$					
25	8.87	8.83	0.816	0.998	3.54
35	10.33	6.12	0.812	0.999	1.21
40	15.38	4.66	0.654	0.995	3.28

M = microcapsule, WPC = whey protein concentrate, MG = mesquite gum, MD = maltodextrin DE 10.

6.83 to 15.38 kg H₂O/100 kg d.s. and increased as temperature increased from 25 to 40°C for both microcapsules. M_0 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. Karel^[44] reported that M_0 values for several foods fall within the range of 4 to 11 kg H₂O/100 kg d.s. in the temperature range of 20 to 70°C.

The values of C and K for both microcapsules (Table 2) fell within the range of $5.67 \leq C < \infty$ and of $0.24 < K \leq 1$, which according to Lewicki^[45] properly describe an isotherm mathematically. Though the value of C decreased with increasing temperature for $M_{\text{WPC66\%/MG17\%/MD17\%}}$, it did not show a clear trend with temperature changes for $M_{\text{WPC17\%/MG17\%/MD66\%}}$. Diosady et al.^[39] reported that heat released by an exothermic reaction between adsorbent and adsorbate will lower the system temperature and produce an increase in the value of C , because C is a constant at constant temperature and is related to the heat of adsorption of water on the powders. C is temperature dependent.

The values of K for $M_{\text{WPC17\%/MG17\%/MD66\%}}$ were 0.960, 0.912, and 0.865 at 25, 35, and 40°C and for $M_{\text{WPC66\%/MG17\%/MD17\%}}$ they were 0.816, 0.812, and 0.654 at 25, 35, and 40°C, respectively. The value of K provides a measure of the interactions between the molecules of the vapor water in the multilayers with the adsorbent and tends to fall between the energy value of the molecules in the monolayer and that of liquid water. A value of K below 1 indicates a less structured state of the adsorbate in the multilayers or GAB layers. The values of K for both of our microcapsules fell within the range of K values reported for GA (0.841, 0.778, and 0.740); MG (0.843, 0.980, and 1.0); and MD (0.899, 0.902, and 0.889) at the same temperatures,^[41] microencapsulated peppermint oil in MD-DE10 (0.946, 0.989, and 1.00); MD-DE20 (0.930, 0.991, and 1.00); and MD-DE30 (0.918, 0.988, and 1.00) matrices at 15, 25, and 35°C, respectively;^[46] and spray-dried yogurt powder (0.462).^[47]

The differential enthalpies (ΔH_{dif}) of the microcapsules were obtained from the slope of the $\ln a_w$ versus $1/T$ plots presented in Fig. 2. $M_{\text{WPC17\%/MG17\%/MD66\%}}$ presented ΔH_{dif} values that were negative within the entire water content and temperature range considered, whereas $M_{\text{WPC66\%/MG17\%/MD17\%}}$ showed ΔH_{dif} values that were positive in the moisture content interval from 1 to 5 kg H₂O/100 kg d.s., which became negative at moisture contents above 5 kg H₂O/100 kg d.s. Negative enthalpy values confirmed the existence of strong attractive forces between the microcapsule's surface and water. A maximum in the $-\Delta H_{\text{dif}}$ values was presented at 36.55 kJ/mol for a water content of 7.0 kg H₂O/100 kg d.s. for $M_{\text{WPC17\%/MG17\%/MD66\%}}$ and at 11.33 kJ/mol for a water content of 12.0 kg H₂O/100 kg d.s. for $M_{\text{WPC66\%/MG17\%/MD17\%}}$.

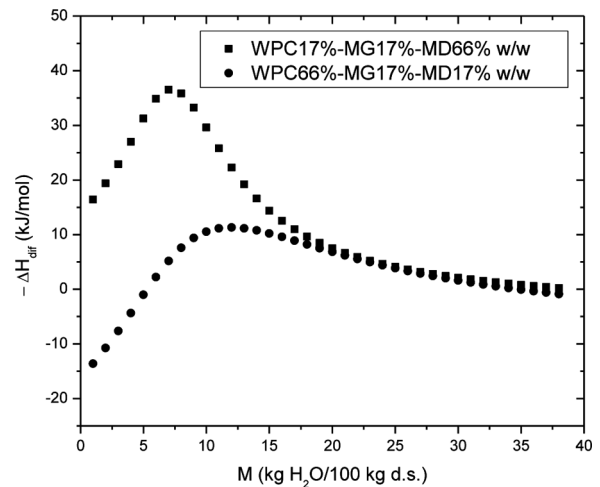


FIG. 2. Differential enthalpy for $M_{\text{WPC17\%/MG17\%/MD66\%}}$ and $M_{\text{WPC66\%/MG17\%/MD17\%}}$.

Microcapsules may exhibit active sites with different binding energies on their surface,^[39] but water molecules are sorbed preferentially onto active sites with the forces producing the most negative ΔH_{dif} values. The maximum enthalpy value indicates the covering of the strongest binding sites and greater water–solid interactions. The covering of less active adsorption sites and the formation of multilayers is manifested by the decrease in enthalpy as water content increases (Fig. 3). Pérez-Alonso et al.^[41] reported that MD-DE10 exhibited a completely different $-\Delta H_{\text{dif}}$ versus moisture content behavior than MG and GA on their own. Though MG and GA showed a maximum in $-\Delta H_{\text{dif}}$, MD-DE10 showed a high initial $-\Delta H_{\text{dif}}$ value (which was higher than the maximum exhibited by MG or GA) that continuously decreased with increasing

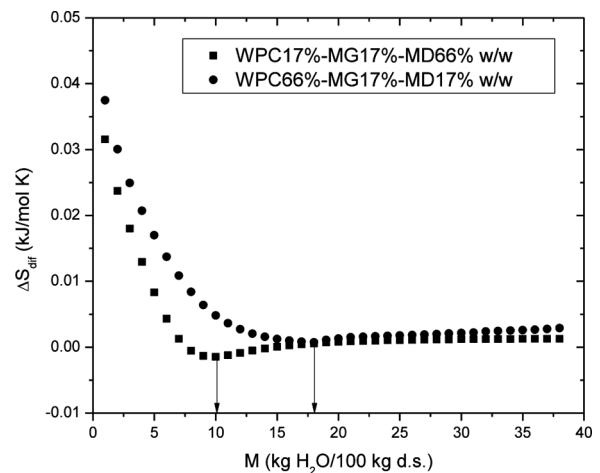


FIG. 3. Differential entropy for $M_{\text{WPC17\%/MG17\%/MD66\%}}$ and $M_{\text{WPC66\%/MG17\%/MD17\%}}$ as a function of moisture content at 35°C.

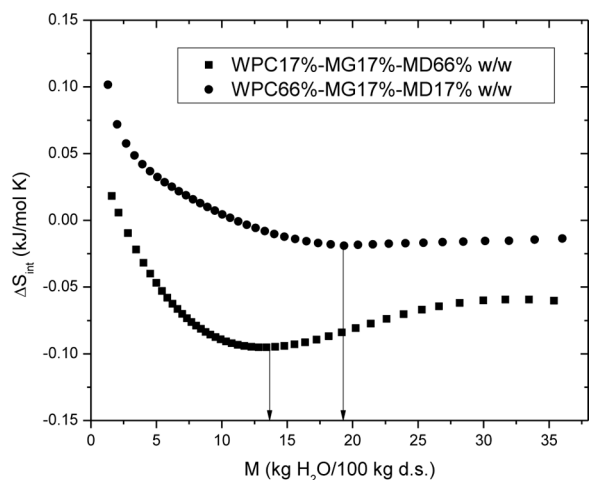


FIG. 4. Integral entropy for $M_{\text{WPC17\%/MG17\%/MD66\%}}$ and $M_{\text{WPC66\%/MG17\%/MD17\%}}$ as a function of moisture content at 35°C.

moisture content. Thus, it seems that in $M_{\text{WPC17\%-MG17\%-MD66\%}}$, where MD is the preponderant wall material in the blend, the $-\Delta H_{\text{dif}}$ maximum was higher and also the material–water interactions.

Figure 4 shows the differential entropy (ΔS_{dif}) as a function of moisture content at 35°C. Differential entropy had a minimum at ~ 10.0 kg $\text{H}_2\text{O}/100$ kg d.s. and ~ 17.8 kg $\text{H}_2\text{O}/100$ kg d.s. for $M_{\text{WPC17\%-MG17\%-MD66\%}}$ and $M_{\text{WPC66\%-MG17\%-MD17\%}}$, respectively. The ΔS_{dif} values were not similar to the GAB monolayer values ($M_0 = 8.78$ kg $\text{H}_2\text{O}/100$ kg d.s. for $M_{\text{WPC17\%-MG17\%-MD66\%}}$ and $M_0 = 10.33$ kg $\text{H}_2\text{O}/100$ kg d.s. for $M_{\text{WPC66\%-MG17\%-MD17\%}}$). A similar trend was exhibited at 25 and 40°C by both microcapsules.

ΔS_{dif} does not mean order or disorder of the total system. ΔS_{dif} represents the algebraic sum of the integral entropy at a particular hydration level plus the change of order or disorder after new water molecules are adsorbed by the system at the same hydration level. If the values of moisture content corresponding to minimum integral entropy (ΔS_{int}) and minimum differential entropy are

different, this particular hydration level at the minimum differential entropy cannot be considered as the maximum stability point, because not all available active sites have been occupied at that particular moisture content. Therefore, it is possible to obtain, after this point, lower differential changes that provide a better ordering of the water molecules adsorbed on the microcapsules. The moisture content at the minimum differential entropy in this case was different from the GAB monolayer values because the maximum entropy change was provoked by the water sorption on the most active sites.

Figure 4 shows the variation in the integral entropy with moisture content at 35°C for the AEO microcapsules. As the powders adsorbed moisture, the entropy diminished to a minimum point that is considered as that of maximum stability, because it is where the water molecules achieve a more ordered arrangement within the solid. The minimum integral entropy value found at 35°C was 13.43 kg $\text{H}_2\text{O}/100$ kg d.s. for $M_{\text{WPC17\%-MG17\%-MD66\%}}$ and 19.34 kg $\text{H}_2\text{O}/100$ kg d.s. for $M_{\text{WPC66\%-MG17\%-MD17\%}}$.

This same trend in the integral entropy vs. moisture content has been observed for MG, GA, sugar beetroot, green whole coffee beans, and ethyl acetate–decaffeinated beans.^[41,48–50] The minimum entropy can be interpreted as the moisture content of the monolayer.^[13,31] This minimum value is expected to arise where strong bonding occurs between adsorbent and adsorbate, which corresponds to less water being available for spoilage reactions. It can also be seen from Fig. 4 that the moisture content corresponding to the minimum integral entropy value for $M_{\text{WPC17\%-MG17\%-MD66\%}}$ to achieve maximum stability was greater than that corresponding to the GAB monolayer (8.78 kg $\text{H}_2\text{O}/100$ kg d.s.). The same occurred for $M_{\text{WPC66\%-MG17\%-MD17\%}}$ (10.33 kg $\text{H}_2\text{O}/100$ kg d.s.). The $M_{\text{WPC17\%-MG17\%-MD66\%}}$ exhibited the lowest minimum integral entropy, so it may be considered as a better wall material than $M_{\text{WPC66\%-MG17\%-MD17\%}}$. The conditions for maximum stability of both microcapsules derived from the thermodynamic analysis are shown in Table 3. As can be appreciated, the water activity (0.45) where

TABLE 3

Conditions of maximum stability for microencapsulated allspice essential oil in biopolymer matrices of different proportions with wall-to-core material ratio of 4:1

T (°C)	$M_{\text{WPC17\%-MG17\%-MD66\%}}$		$M_{\text{WPC66\%-MG17\%-MD17\%}}$	
	M (kg $\text{H}_2\text{O}/100$ kg d.s.)	a_w	M (kg $\text{H}_2\text{O}/100$ kg d.s.)	a_w
25	13.79	0.551 ± 0.016^b	19.63	0.713 ± 0.021^c
35	13.43	0.450 ± 0.014^a	19.34	0.657 ± 0.020^b
40	15.11	0.444 ± 0.013^a	18.71	0.591 ± 0.018^a

Values in the same column with different superscripts are significantly different ($p < 0.05$) M = microcapsule, WPC = whey protein concentrate, MG = mesquite gum, MD = maltodextrin DE 10.

$M_{WPC17\%-MG17\%-MD66\%}$ was found to be more stable coincided with that determined for red chilli oleoresin microcapsules encapsulated in a biopolymer matrix made by the same hydrocolloids in the same proportion, both experiments done at 35°C, and for core-to-wall material ratio of 1:4.^[17] Beristain et al.^[30] found that orange peel oil entrapped in pure MG microcapsules exhibited best physical stability at $a_w = 0.436$ at $T = 35^\circ\text{C}$.

CONCLUSIONS

The magnitude of the difference between the mean particle size of the microcapsules and that of the emulsions from which they were originated seems to be closely inter-related to the allspice essential oil encapsulation efficiency. The thermodynamic analysis of sorption isotherms allowed determination of the best storage conditions (water activity and temperature) for providing long-term physical stability to allspice essential oil entrapped in matrices made up by the same biopolymer blends but in different proportions. This work shows that the establishment of suitable storage conditions for dry products may vary considerably, even when possessing very similar composition, and contributes to the knowledge for improving the shelf life and functionality of dry products.

NOMENCLATURE

a_w	Water activity
C	Guggenheim coefficient
c'	Equation constant (2)
E	Mean relative deviation modulus
E_a	Activation energy (kJ/mol)
EE	Encapsulation efficiency (kg eugenol retained/100 kg eugenol incorporated in microcapsules)
E_M	Eugenol in microcapsules
ΔG	Free energy for water adsorption (kJ/mol)
ΔH_{dif}	Molar differential enthalpy (kJ/mol)
ΔH_{int}	Molar integral enthalpy (kJ/mol)
H_l	Partial molar enthalpy of adsorbed water at constant temperature and pressure (kJ/mol)
H_s	Molar enthalpy of water adsorbed of the microcapsule (kJ/mol)
h_l	Molar differential enthalpy of water absorbed in the microcapsule (kJ/mol) Eq. (6)
h_m	Total heat sorption of the first layer (kJ/mol)
h_n	Total heat of sorption of the multilayers (kJ/mol)
h_1	Heat of condensation of pure water (kJ/mol) Eq. (3)
K	Coefficient correcting properties of the multilayer molecules with respect to the bulk liquid
k	Eugenol degradation rate constant (weeks^{-1})
k'	Equation (3) constant
M	Equilibrium moisture content (kg water/100 kg dry solids)
M_{Ei}	Predicted moisture content at that observation i

M_i	Moisture content at observation i
M_0	Monolayer water content (kg water/100 kg dry solids)
N_1	Moles of water adsorbed in the microcapsule
n	Number of observations
p	Equilibrium pressure (N/m^2)
p_0	Vapor pressure of pure water (N/m^2),
q_{st}	Net isosteric heat sorption (kJ/mol)
R	Universal gas constant (kJ/mol K)
S	Entropy of water adsorbed in the microcapsule (kJ/mol K)
ΔS_{dif}	Molar differential entropy (kJ/mol K)
ΔS_{int}	Molar integral entropy (kJ/mol K)
S_l	Molar entropy of pure water in equilibrium with the vapor (kJ/mol K)
S_s	Integral entropy of water adsorbed in the microcapsule (kJ/mol K)
s_l	Molar differential entropy of water adsorbed in the microcapsule (kJ/mol K)
T	Absolute temperature (K)
$t_{1/2}$	Time of half-life of eugenol in microcapsules (weeks)
W_{ap}	Molecular weight of the adsorbent (kg/mol)
W_v	Molecular weight of water (kg/mol)

Greek Symbols

μ_a	Chemical potential of the adsorbent in the condensed phase (kJ/mol)
μ_{ap}	Chemical potential of the pure adsorbent (kJ/mol)
Φ	Diffusion pressure or surface potential of the microcapsule (kJ/mol)

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