STORAGE STABILITY AND PHYSICOCHEMICAL PROPERTIES OF PASSION FRUIT JUICE MICROCAPSULES BY SPRAY-DRYING

ESTABILIDAD DURANTE EL ALMACENAMIENTO Y PROPIEDADES FISOCOQUÍMICAS DE MICROCÁPSULAS DE JUGO DE MARACUYÁ OBTENIDAS MEDIANTE SECADO POR ASPERSIÓN

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Abstract

The aim of this work was to microencapsulate passion fruit juice (PFJ) by spray-drying in two different biopolymers blends: Gum Arabic-mesquite gum-maltodextrin DE-10 (GA17-MG66-MD17 and GA17-MG-17-MD66), yielding the microcapsules $M_{GA17\text{-}MG66\text{-}MD17}$ and $M_{GA17\text{-}MG17\text{-}MD66}$. The spray-dried passion fruit microcapsules were analyzed for physicochemical properties (moisture content, water activity, powder particle size), quality properties (hygroscopicity, dispersibility, rehydration time), and reconstituted product properties (total color change and vitamin C retention). The minimum integral entropy of the microcapsules was determined at 25, 35, and 40 °C, and the resulting water activities (a_W) were 0.447, 0.505, 0.629 for $M_{GA17\text{-}MG66\text{-}MD17}$ and 0.383, 0.414, 0.605 for $M_{GA17\text{-}MG17\text{-}MD66}$, respectively. These temperatures-a_W sets were considered as the most adequate conditions for achieving maximum storage stability of the microcapsules. The best vitamin C retention level occurred at 25 °C, a_W = 0.447 for $M_{GA17\text{-}MG66\text{-}MD17}$, and at 25 °C, a_W = 0.383 for $M_{GA17\text{-}MG17\text{-}MD66}$.

Keywords: passion fruit juice, spray drying, microencapsulation, sorption isotherms, water activity, vitamin C.

Resumen

El objetivo de este trabajo fue microencapsular jugo natural de maracuyá (PFJ) mediante secado por aspersión en dos mezclas de biopolímeros en distintas proporciones: Goma Arábiga-goma de mezquite-maltodextrina DE-10 (GA17-GM66-MD17 and GA17-GM-17-MD66), produciendo dos tipos de microcápsulas $M_{GA17\text{-}MG66\text{-}MD17}$ y $M_{GA17\text{-}MG17\text{-}MD66}$. Las microcápsulas de PFJ fueron analizadas determinando sus propiedades fisicoquímicas (contenido de humedad, actividad de agua, tamaño promedio de partícula), propiedades de calidad (higroscopicidad, dispersabilidad, tiempo de rehidratación), y propiedades de reconstitución de las microcápsulas (cambio de color total del jugo, retención de vitamina C en el jugo). La entropía mínima integral de las microcápsulas se determinó a 25, 35 y 40 °C, y las actividades de agua resultantes (a_W) fueron de 0.447, 0.505, 0.629 para $M_{GA17\text{-}MG66\text{-}MD17}$ y de 0.383, 0.414, 0.605 para $M_{GA17\text{-}MG17\text{-}MD66}$, respectivamente. El conjunto de valores temperatura-a_W fueron considerados como las condiciones más adecuadas para alcanzar la estabilidad máxima de las microcápsulas. Las mejores condiciones de retención de vitamina C ocurrieron a 25 °C y una a_W = 0.447 para $M_{GA17\text{-}MG66\text{-}MD17}$, y a 25 °C, a_W = 0.383 para $M_{GA17\text{-}MG17\text{-}MD66}$.

Palabras clave: jugo natural de maracuyá, secado por aspersión, microencapsulación, isotermas de adsorción, actividad de agua, vitamina C.

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1 Introduction

The genus *Passiflora* comprises approximately 450 species, but only a few are commercially exploited. *Passiflora edulis v flavicarpa*, usually called passion fruit, is the best known among them (Ferreres *et al.*, 2007). This fruit is originated in America and is a tropical fruit. In Mexico passion fruit, known as "Maracuyá" is a seasonal fruit and it is not available all year round. Besides, in Mexico only a very small proportion of the yearly harvest reaches the international market, mainly due to the lack of a good method of preservation that facilitates transportation and storage. Drying as a preservation method may be an alternative for a better utilization of passion fruit, creating new varieties of products and make available throughout the year. Spray drying can be used to convert passion fruit juice into stable powder with new possibilities of industrial applications (i.e., beverages, soups, ice cream), should have instant properties and served as a source of vitamin C for addition into food products (Talcott *et al.*, 2003; Rodríguez-Hernández *et al.* 2005; Quek *et al.*, 2007).

Biopolymers used as wall materials for food ingredients encapsulation by spray drying include gum Arabic (Pérez-Alonso *et al.*, 2009; Pitalua *et al.*, 2010), mesquite gum (Rodríguez-Huezo *et al.*, 2004; Pérez-Alonso *et al.*, 2008) and maltodextrins (Martinelli *et al.*, 2007; Tonon *et al.*, 2010). Gum Arabic is a complex heteropolysaccharide with a highly ramified structure, with a main chain formed of D-galactopyranose, units joined by β-D-glycosidic bonds $(1 \rightarrow 3)$. Side chains with variable chemical structures formed from D-galactopyranose, L-rhamnose, L-arabino-furanose, and D-galacturonic acid linked to the main chain $\beta(1 \rightarrow 6)$ bonds. Gum Arabic has been used as an encapsulating material in microencapsulation by spray drying, mainly because of its good emulsifying capacity and low viscosity in aqueous solution, which aids the spray-drying process (Martinelli *et al.*, 2007).

Mesquite gum is a very high molecular weight neutral salt of an acidic branched polysaccharide made up by a backbone of residues of (1-3) linked β-D-galactose, and (1-6) side chains containing L-arabinose, L-rhamnose, β-D-glucuronate and 4-o-methyll-β-D-glucuronate, having a small amount of protein ($2.7 \pm 0.06\%$) attached to the polysaccharide moiety, which is largely responsible for its excellent emulsifying and film forming capacity (Orozco-Villafuerte *et al.*, 2003).

Maltodextrins consist of β-D-glucose units linked mainly by glycosidic bonds $(1 \rightarrow 4)$ and are usually classified according to their dextrose equivalency (DE). The DE of a maltodextrin determines its reducing capacity and is inversely related to its average molecular weight. Maltodextrins are mainly used in materials that are difficult to dry-such as fruit juices, flavorings, and sweeteners and to reduce stickness and agglomeration problems during storage, thereby improving product stability (Martinelli *et al.*, 2007).

It is hoped that by doing this, the microcapsules can be potentially incorporated in dry form into the functional foods (instant beverages, cake mixes, gelatine desserts, chewing gums, pet foods, breakfast cereal, etc.).

The aim of this work was to study the feasibility of spray drying of passion fruit juice: i) Determine the physicochemical properties of the microcapsules produced; ii) determine the quality properties; iii) evaluate reconstituted product properties; and iv) establish the most suitable storage conditions for microcapsules.

2 Materials and methods

2.1 Materials

Fresh passion fruits were collected from a plantation located in the city of Poza Rica, Veracruz, México. Gum Arabic (*Acacia senegal*) (GA) purchased from Industria Ragar, S.A. de C.V. (Mexico City, Mexico), mesquite gum (MG) was 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), and maltodextrin DE-10 (MD) was obtained from Complementos Alimenticios S.A. de C.V. (Maltadex^{TM} 10, Naucalpan, State of Mexico, México) and were used as protective colloids. All chemicals used in this study were reagent grade. All the water used in the experiments was bidistilled.

2.2 Extraction and analysis of the passion fruit juice (PFJ)

The fruits were washed and cut into halves, discarding the skins and keeping only the pulp. The pulp was prepared with a solution enzymatic of the pectinases and hemicellulases (DSM Food Specialties Mexicana, Naucalpan, State of Mexico, México) (0.1 mL of enzymatic solution/kg pulp) (Rodríguez-Hernández *et al.*, 2005). This treatment was carried out at room

temperature ($\sim$ 18 °C) for 1 h under static conditions. The juice was filtered through a Tyler # 9 (2000 μm) sieve in order to eliminate solids in suspension, facilitating the product's passage through the nozzle atomizer. Finally the juice was stored in a freezing chamber and later defrosted at the room temperature right before the experiments.

Analyses of the PFJ were carried out to determine the physicochemical properties (pH, total soluble solids, color, and vitamin C content). The pH of the PFJ was measured using pH meter (Metrohm, model 744, Riverview, FL, USA). The total soluble solids content of the juice was measured using the Atago Hand-Held refractometer (model ATC-IE, Brix 0-32%, Bellevue, WA, USA). The parameters of lightness (L_0^*), redness (a_0^*) and yellowness (b_0^*) of the passion fruit juice natural were determined with a Hunter Lab (MS-4,500 L. Format 2. 1/4 P65/10°, Reston, VA, USA) colorimeter. Vitamin C was determined by titration using 2,6-dichloro-indophenol (Sigma Aldrich, Toluca, Estado de México, México) as described in Official Methods of Analysis (1980). All the measurements were done in triplicate.

2.3 Preparation and spray-drying of the PFJ filtered pulp

Based on the results obtained by Pérez-Alonso *et al.* (2003), two different biopolymers blends were selected: GA17%-MG66%-MD17% which displayed high activation energy (30.6 kJ/mol) and GA17%-MG17%-MD66% which displayed low activation energy (19.9 kJ/mol) (Pérez-Alonso *et al.*, 2003) and should provide protection and retention vitamin C to the microencapsulated PFJ. Both biopolymer blends were dissolved into the PFJ to a total solids content of 30% w/w and stirred to homogeneity with an Ultra-Turrax T50 basic homogenizer (IKA-WERKE Works Inc., Wilmington, NC, USA) at a speed of 5200 r.p.m. for 8 min. The solutions were then fed at a rate of 40 mL/min to a Nichols/Niro spray-drier (Turbo Spray PLA, NY, USA) operated with inlet temperature of 135 $\pm$ 5 °C, outlet temperature of 80 $\pm$ 5 °C and injecting compressed air at 4 bar. The spray-dried powders ($M_{GA17-MG66-MD17}$ and $M_{GA17-MG17-MD66}$) were collected, kept in plastic bags wrapped with aluminum foil. Spray drying of each formulation was done in triplicate.

2.4 Physicochemical properties of the spray-dried microcapsules

The physicochemical properties of the spray-dried microcapsules were analysed for their moisture content, water activity and microcapsules particle size.

2.4.1 Moisture content

The moisture content was determined according to the AOAC method (1980). Triplicate samples of $M_{GA17-MG66-MD17}$ and $M_{GA17-MG17-MD66}$ ($\sim$ 1 g) were weighed and then dried in a vacuum oven at 70 °C for 24 h. The samples were removed from the oven, cooled in a desiccator and weighed. The drying and weighing processes were repeated until constant weigh were obtained.

2.4.2 Water activity

Measurement of water activity was carried out using an Aqualab water activity meter with temperature compensation (model series 3 TE, Decagon Devices, Inc., Pullman, WA, USA). Triplicate samples ($\sim$ 0.50 g) of $M_{GA17-MG66-MD17}$ and $M_{GA17-MG17-MD66}$ were analysed and the mean was recorded.

2.4.3 Microcapsules particle size

The volume fraction-lenght mean size ($d_{4,3}$) of microcapsules was determined with a Mastersizer 2000 (Malvern Instruments, Ltd., Malvern, Worcetershire, England), using water as dispersant.

2.5 Quality properties of the spray-dried microcapsules

Some properties can express the quality of food microcapsules, such as hygroscopicity, dispersibility and time rehydration. The hygroscopicity and dispersibility were determined as indicated by Martinelli *et al.* (2007) and rehydration time of the microcapsules was determined as indicated by Quek *et al.* (2007). The rehydration time of the microcapsules was determined immediately after spray drying process.

2.6 Rehydrated microcapsules properties

2.6.1 2.6.1. Total color change of the rehydrated microcapsules

The microcapsules samples were rehydrated to the same moisture content as the natural juice. The quantity of bidistilled water/g of microcapsules was calculated to obtain exactly 14.0 ± 0.5 °Brix (20 g H_2O/g microcapsule). The parameters of color of the rehydrated microcapsules were determined as section 2.2. Total color change (ΔE) of the rehydrated microcapsules was obtained with the following expression (Rodríguez-Hernández *et al.*, 2005):

$$\Delta E = \left(\Delta L^{*2} + \Delta a^* 2 + \Delta b^{*2}\right)^{0.5} \tag{1}$$

where Δ indicates the difference between the initial and final L^*, a^* and b^* parameters.

2.6.2. Vitamin C retention in rehydrated microcapsules

Vitamin C was considered in this work as an index to evaluate the quality retention of the PFJ after the spray-drying process. It is generally observed that, if the vitamin C is well retained, the other nutrients are also well retained (Uddin *et al.*, 2002). Vitamin C was determined by titration using 2,6-dichloro-indophenol (Sigma Aldrich, Toluca, Estado de México, México) as described in Official Methods of Analysis (1980).

2.7 Sorption isotherms of microcapsules

$M_{GA17-MG66-MD17}$ and $M_{GA17-MG17-MD66}$ were put into glass Petri dishes, taking care that the microcapsules covered completely and homogeneously the dishes surface. The dishes were then introduced into glass desiccators containing P_2O_5 as desiccant, at room temperature (18 ± 2 °C) for 3 weeks in order to reduce to a minimum water activity (~0.02) of the microcapsules. The adsorption isotherms were determined by the gravimetric method described by Lang *et al.* (1981). Approximately 1.0 ± 0.1 g of the microcapsules of $M_{GA17-MG66-MD17}$ and $M_{GA17-MG17-MD66}$ were put into small glass desiccators of 10 cm diameter which contained saturated solutions of different salts that provided water activities (a_W) in the range of 0.11-0.85 (Labuza *et al.*, 1985). Filter paper (Whatman No. 1) was placed above the saturated salt solutions, in a perforated plate used as support for the powders for allowing moisture transmission. Five desiccators with each type

of microcapsule for each saturated solution salt were placed into forced convection drying oven (Riossa, model E-51, Mexico City, Mexico) at three temperatures: 25, 35 and 40 °C. The microcapsules were weighed with an Ohaus electronic balance (model AP210, Pine Brook, NJ, USA) every five 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, USA). Longer drying times did not produce sample weight decrease by more than 0.1 mg.

The Guggenheim-Anderson-De Boer (GAB) equation is a model with three parameters that have physical meaning, and is recognized as the most versatile sorption model available for the sorption of food. It is mathematically expressed as (Pérez-Alonso *et al.*, 2009):

$$M = \frac{M_0 C K a_W}{(1 - Ka_w)(1 - Ka_w + CKa_w)} \tag{2}$$

where M is the equilibrium moisture content (kg water/100 kg dry solids); M_0 is the monolayer water content (kg water/ 100 kg dry solids), a_W is the water activity, and C is the Guggenheim constant, given by:

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

and K is the constant correcting properties of the multilayer molecules with respect to the bulk liquid, and given by:

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

The parameters were estimated by fitting the mathematical model to the experimental data, using non-linear regression with Origin version 8.5 Scientific Graphing and Analysis Software (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 equation (McLaughlin & Magee, 1998):

$$E = \frac{100}{N} \sum \frac{|M_i - M_{Ei}|}{M_i} \tag{5}$$

where M_i is the moisture content at observation i; M_{Ei} is the predicted moisture content at that observation and n is the number of observations. It is generally assumed that a good fit is obtained when $E < 5\%$.

2.8 Thermodynamic properties of the microcapsules

The determination of the differential and integral (enthalpy and entropy) thermodynamic properties, 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.

2.9 Statistical analyses

Data were analyzed using a one way analysis of variance (ANOVA) and a Tukey test for a statistical significance $P \leq 0.05$, using the SPSS Statistics 19.0 (IBM Corporation, N.Y., U.S.A.). All experiments were done in triplicate.

3 Results and discussion

3.1 Analysis of the passion fruit juice (PFJ)

The physicochemical properties of natural passion fruit juice used for spray drying. It can be seen that the passion fruit juice has a low pH value (3.8), which inhibits microbial growth. Total soluble solids were 14 °Brix and the content of vitamin C of PFJ was 16 ± 0.80 mg/100 mL juice. The content of vitamin C is an indicator of quality of the juice, and in the spray drying process; vitamin C plays an important role in assessing the degree of protection by encapsulating agent's juice. The juice has a bright yellow color as indicated by the values $L_0^* = 42.36 \pm 2.12$, $a_0^* = 9.16 \pm 0.46$ and $b_0^* = 17.53 \pm 0.88$. Color parameters are an important feature reflecting the sensory quality of the juices.

3.2 Physicochemical properties of the spray-dried microcapsules

Table 1 shows the physicochemical properties of the spray-dried microcapsules. The initial moisture content ranged from 4.82-5.51% drying base. The moisture content depends on the wall material, it is reported that when wall material reaches a moisture content $< 7\%$, the diffusion coefficient of water is reduced, and this decreases its movement through the dry matrix (Reineccius, 2004). Water activity is different from moisture content as it measures the availability of free water in a food system that is responsible for any biochemical reactions, whereas the moisture content represents the water composition in a food system. From the results (Table 1), the water activities of the powders were in the range of 0.294-0.328. Generally, foods with $a_W < 0.6$ are considered to be microbiologically more stable (Quek *et al.*, 2007). The volume fraction-lenght mean size ($d_{4,3}$) of microcapsules was found to be slightly larger when the mesquite gum is found in higher composition in the biopolymer blends, this is probably due to mesquite gum has a considerably greater molecular weight (∼ 2, 120, 000 Da) (Vernon-Carter *et al.*, 1998) than GA (∼ 1, 000, 000 Da) (Fenyo & Vandevelde, 1990) and exhibits a highly branched spherical structure that tend to form fine, dense, two dimensional skins immediately upon drying (Pérez-Alonso *et al.*, 2003). Rodríguez-Huezo *et al.* (2004) microencapsulated carotenoids with GA-MG-MD biopolymers blend as wall material at different concentrations producing microcapsules with d_{43} between 25 and 35 μm.

3.3 Quality properties of the spray-dried microcapsules

Table 2 shows the quality properties of the spray-dried microcapsules. The hygroscopicity was very high for both types of microcapsules, this can be explained by the fact that biopolymers were used as encapsulating agents have a hydrophilic character, besides, did not

Table 1. Physicochemical properties of the microcapsules of passion fruit juice

Microcapsule	Moisture content (%)	a_W	$d_{4,3}$ (μm)
$M_{GA17 - MG66 - MD17}$	5.51 ± 0.25	0.328 ± 0.01	28 ± 1.26
$M_{GA17 - MG17 - MD66}$	4.82 ± 0.19	0.294 ± 0.01	22 ± 0.88

M = Microcapsule, GA = Gum Arabic, MG = Mesquite Gum, MD = Maltodextrin DE-10
a_W = Water activity, $d_{4,3}$ = Volume fraction-lenght mean size

Table 2. Quality properties of the microcapsules of the passion fruit juice

Microcapsule	Higroscopicity (%)	Dispersability (%)	Rehydration Time (s)
$M_{GA17 - MG66 - MD17}$	82.35 ± 3.71	95.41 ± 4.29	39 ± 1.75
$M_{GA17 - MG17 - MD66}$	79.07 ± 3.16	88.07 ± 3.52	43 ± 1.72

M = Microcapsule, GA = Gum Arabic, MG = Mesquite Gum, MD = Maltodextrin DE-10

Table 3. Physicochemical properties of the reconstituted microcapsules of the passion fruit juice at 25 °C

Microcapsule	a_W	Vitamin C retention (%)	Total color change (ΔE)
$M_{GA17 - MG66 - MD17}$	0.328 ± 0.01	64.80 ± 2.59	6.07 ± 0.27
$M_{GA17 - MG17 - MD66}$	0.294 ± 0.01	59.86 ± 2.69	5.21 ± 0.21

M = Microcapsule, GA = Gum Arabic, MG = Mesquite Gum, MD = Maltodextrin DE-10
a_W = Water activity.

show a high degree of caking (visual evidence), because of the percentage of dispersability was high, and therefore, the rehydration time was less than one minute to the amount of microcapsule rehydrated (1.0 g), it follows that the passion fruit juice microencapsulation can be used as an instant powder beverage.

3.4 Rehydrated microcapsules properties

Table 3 shows the rehydrated microcapsules properties at 25 °C. The passion fruit juice obtained from the rehydrated microcapsules with higher composition of mesquite gum $M_{GA17-MG66-MD17}$ had a high retention of vitamin C and greater total color change compared to the microcapsules prepared with high composition of maltodextrin $M_{GA17-MG17-MD66}$. This can be explained in terms of the ternary biopolymers blend (GA17-MG66-MD17) has been studied and validated as a polymeric membrane to form fine, dense, two-dimensional skins higher robust and act as barrier against degradation phenomena lipid oxidation than the ternary biopolymers blend (GA17-MG17-MD66) (Pérez-Alonso *et al.*, 2003).

3.5 Sorption isotherms of microcapsules

The experimental sorption isotherms data at 20, 35, and 40 °C for both microcapsules fitted very well the GAB model, and the resulting parameters values are given in Table 4. The mean relative deviation modulus value was less than 5% for all the experimental temperatures and the coefficient of determination R^2 was over 0.97 for both samples. The value of the monolayer (M_0) fell within the range of 6.20 to 15.69 kg H2O/100 kg dry solids and increased as temperature increased from 25 to 40 °C for both microcapsules. M_0 values are 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.

The values of C and K for both microcapsules (Table 4) fell within the range of $5.67 \leq C < \infty$ and of $0.24 < K \leq 1$, which according to Lewicki (1997) describe properly an isotherm mathematically. While the value of C decreased with increasing temperature for both microcapsules. Diosady *et al.* (1996) reported that heat released by exothermic reaction between adsorbent and adsorbate will lower the system temperature, and produce an increase in the value of C, as 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 value of K provides a measure of the interactions between the molecules of the vapour 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

Table 4. Estimated parameters of the GAB equation for passion fruit juice microcapsules

T (°C)	M_0 (kg H$_2$O/100 kg d.s.)	C	K	R^2	E (%)
M$_{GA17 - MG66 - MD17}$					
25	6.42	10.92	0.940	0.990	3.85
35	10.78	6.20	0.803	0.993	3.40
40	12.85	5.91	0.718	0.992	3.77
M$_{GA17 - MG17 - MD66}$					
25	8.20	15.69	0.837	0.989	4.49
35	10.31	14.69	0.762	0.986	3.92
40	12.07	13.76	0.687	0.970	4.27

M = Microcapsule, GA = Gum Arabic, MG = Mesquite Gum, MD = Maltodextrin DE-10
M_0 = Monolayer water content (kg water/100 kg dry solids), C = Gugenheim constant,
K = Constant correcting properties of the multilayer molecules with respect to the bulk
liquid, R^2 = Coeficient of determination, E = Mean relative deviation modulus.

K below 1 indicates a less structured state of the adsorbate in the multilayers or GAB layers. The values of K for both 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 DE10 (0.899, 0.902 and 0.889) at the same temperatures (Pérez- Alonso *et al.*, 2006), microencapsulated lemon juice in MD-DE20 (0.960, 0.914, and 0.971); and GA (0.926, 0.975, and 0.954) matrices at 20, 30 and 40 °C, respectively (Martinelli *et al.*, 2007).

3.6 Thermodynamic properties of the microcapsules

The differential enthalpies (ΔH_{dif}) of the microcapsules plotted as function of water content are presented in Fig. 1. All ΔH_{dif} values were negative within the entire water content and temperature range considered. Negative enthalpy values confirmed that strong attractive forces existed between the microcapsules surface and water. A maximum in the $-\Delta H_{dif}$ values was presented at 23.83 kJ/mol for a water content of 8.40 kg H$_2$O/100 kg d.s. for M$_{GA17-MG66-MD17}$ and at 26.79 kJ/mol for a water content of 8.40 kg H$_2$O/100 kg d.s. for M$_{GA17-MG17-MD66}$, respectively.

Microcapsules may exhibit active sites with different binding energies on their surface (Rizvi & Benado, 1984), 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 increasing ΔH_{dif} corresponds to

an endothermic process that may be associated with swelling of the carbohydrate polymer matrix that exposes new active sites, where new water molecules can be adsorbed by an exothermic process that compensates the endothermic heat. The covering of less active adsorption sites and the formation of multi-layers is manifested by the decrease in enthalpy as water content increases (Fig. 1). Pérez-Alonso *et al.* (2006) reported that MD exhibited a completely different $-\Delta H_{dif}$ versus moisture content behaviour than MG and GA. While MG and GA showed a maximum in $-\Delta H_{dif}$, MD showed a high initial $-\Delta H_{dif}$ value (that was higher than the maximum exhibited by MG or GA) which decreased continuously with increasing moisture content.
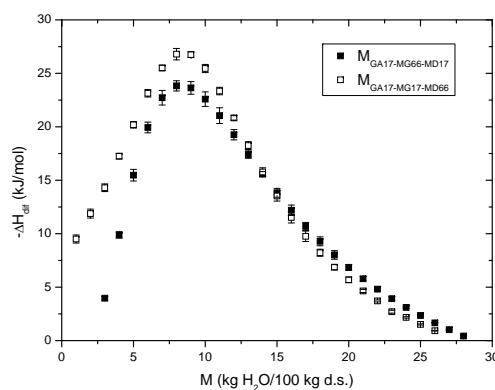

Fig. 1. Differential enthalpy as a function of moisture content for M$_{GA17-MG66-MD17}$ and M$_{GA17-MG17-MD66}$.
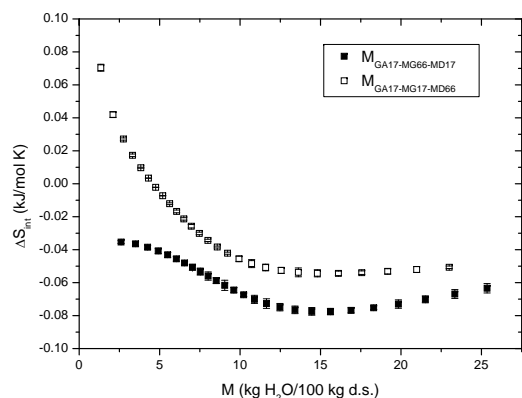
Fig. 2. Integral entropy for $M_{GA17-MG66-MD17}$ and $M_{GA17-MG17-MD66}$ as a function of moisture content at 25 °C.

Fig. 2 shows the variation in the integral entropy with moisture content at 25 °C for the microcapsules. As the microcapsules 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 25 °C was 14.68 ± 0.66 kg H_2O/100 kg d.s. for $M_{GA17-MG66-MD17}$ and 15.58 ± 0.62 kg H_2O/100 kg d.s. for $M_{GA17-MG17-MD66}$.

This same trend in the integral entropy vs. moisture content has been observed for MG, GA (Pérez-Alonso *et al.*, 2006). The minimum entropy can be interpreted as the moisture content of the monolayer. 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. 2 that the moisture content corresponding to the minimum integral entropy value for $M_{GA17-MG66-MD17}$ to achieve maximum stability was greater than that corresponding to the GAB

monolayer (6.42 kg H_2O/100 kg d.s.). The same occurred for $M_{GA17-MG17-MD66}$ (8.20 kg H_2O/100 kg d.s.). This behaviour of the Fig. 2 was the same for the other temperatures (35 and 40 °C). The $M_{GA17-MG66-MD17}$ exhibited the lowest minimum integral entropy, so it may be considered as a better wall material than $M_{GA17-MG17-MD66}$.

The conditions for maximum storage stability of both microcapsules are shown in Table 5. As can be appreciated, that as the temperature increases, so does the water activity increases, and the vitamin C retention decreased. In a general way, the influence of temperature and a_W also play an important role on vitamin C retention of microcapsules passion fruit juice. Factors like ageing of the glassy material (microcapsule), rotational mobility and diffusion for porosity in the structure, as well as the characteristic heterogeneity of microencapsulated systems, can explain the occurrence of chemical reactions in microcapsules and like affect the stability (Slade & Levine, 1991). The decrease in vitamin C retention was much more pronounced for the microcapsules at higher temperatures (35-40 °C) and a_W's (0.505-0.629) for $M_{GA17-MG66-MD17}$, and (35-40 °C) and a_W's (0.414-0.605) for $M_{GA17-MG17-MD66}$. The microcapsules stored at these conditions, possibly were not in the glassy state, which can be the cause of the very lower vitamin C retention, since molecular mobility of the water is much greater, which can accelerate degradation reactions. The best vitamin C retention level occurred at 25 °C, a_W = 0.447 for $M_{GA17-MG66-MD17}$ and at 25 °C, a_W = 0.383 for $M_{GA17-MG17-MD66}$. The lowest minimum integral entropy was exhibited by $M_{GA17-MG66-MD17}$ that has a higher activation energy (30.6 kJ/mol) so it may be considered as a better wall material than $M_{GA17-MG17-MD66}$ that has a lower activation energy (19.9 kJ/mol) (Pérez-Alonso *et al.*, 2003) for protecting JFP.

Table 5. Maximum stability conditions for the microencapsulated passion fruit juice

Microcapsule	T (°C)	M (kg H_2O/100 kg d.s.)	a_W	Vitamin C retention (%)
$M_{GA17 - MG66 - MD17}$	25	14.68 ± 0.66^b	0.447 ± 0.02^b	60.34 ± 2.41^d
	35	14.35 ± 0.65^b	0.505 ± 0.02^c	51.12 ± 2.04^c
	40	14.60 ± 0.66^b	0.629 ± 0.03^d	38.35 ± 1.53^a
$M_{GA17 - MG17 - MD66}$	25	15.58 ± 0.62^b	0.383 ± 0.01^a	56.65 ± 2.55^d
	35	13.24 ± 0.53^a	0.414 ± 0.02^b	48.71 ± 2.19^b
	40	13.60 ± 0.54^a	0.605 ± 0.02^d	35.97 ± 1.62^a

M = Microcapsule, GA = Gum Arabic, MG = Mesquite Gum, MD = Maltodextrin DE-10 a_W = Water activity.

Superscripts with different letters in same column indicate significant differences ($P \leq 0.05$).

Conclusions

The results of this work indicated that the combination of GA-MG-MD worked effectively as protective colloids for the spray drying of the passion fruit juice. The thermodynamic analysis of sorption isotherms allowed to determine the best storage conditions (water activity and temperature) for providing long term physical stability and vitamin C retention to passion fruit juice entrapped in matrices made-up by the same biopolymers 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 instant powder beverages.

Acknowledgment

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