Food Chemistry 259 (2018) 175–180

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Thermodynamic criteria analysis for the use of taro starch spherical aggregates as microencapsulant matrix

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ARTICLE INFO

Keywords:
Starch
Sorption isotherm
Enthalpy
Entropy
Diffusion

ABSTRACT

Spherical aggregates can be obtained from taro starch by spray-drying without using bonding agents. Accurate information about thermal issues of spherical aggregates can provide valuable information for assessing the application as encapsulant. Spherical aggregates of taro starch were obtained by spray-drying and analyzed using dynamic vapour sorption. The use of the Guggenheim, Anderson and de Boer (GAB) model indicated a Type II isotherm pattern with weaker interactions in the multilayer region. Differential enthalpy and entropy estimates reflected a mesoporous microstructure, implying that energetic mechanisms dominate over transport mechanisms in the sorption process. The limitation by energetic mechanisms was corroborated with enthalpy-entropy compensation estimates. The diffusivity coefficient was of the order of $10^{-8}\,m^2{\cdot}s^{-1}$, which is in line with results obtained for common materials used for encapsulation purposes. The thermodynamic properties and the lack of a bonding agent indicated the viability of spherical aggregates of taro starch for encapsulation of bio-compounds.

1. Introduction

Starch spherical aggregates obtained from diverse botanical sources have been considered as suitable structures for microencapsulation purposes. Zhao and Whistler (1994) found that amaranth and small wheat and corn starch granules can lead to spherical aggregates during spray-drying. However, the formation of spherical aggregates required the addition of bonding agents, such as gums and proteins. Tari et al. (2003) studied the ability of small sized starch granules from amaranth (*Amaranthus paniculatus* L.), quinoa (*Chenopodium quinoa* L.), rice (*Oryza sativa* L.) and colocasia (*Colocasia esculenta* L.) in the presence of polysaccharide bonding agents (gum Arabic, carboxymethyl cellulose and carrageenan) to microencapsulate vanilla as a model compound. It was found that amylose content was negatively correlated with the extent of entrapment of vanillin held within the spherical aggregates. Beirão-Da-Costa, Duarte, Moldão-Martins, & Beirão-da-Costa (2011) explored the effect of the presence of bonding agents (CMC and/or gelatin), and of solids content, on the physical characteristics of spherical aggregates from rice starch. Interestingly, it was found that the concentration of the bonding agent did not significantly affect the porosity of spherical aggregates. Gonzalez-Soto, de la Vega, García-Suarez, Agama-Acevedo, and Bello-Pérez (2011) reported that taro starch had the ability to form spherical aggregates without the addition of bonding agents. Notably, Gonzalez-Soto et al. (2011) only reported the method for obtaining spherical aggregates from taro starch. In fact, these authors only reported the formation of spherical aggregates as a peculiarity of taro starch, without further exploring potential applications of such structures. However, the peculiarity of taro starch spherical aggregates indicates that it could be used as wall material in encapsulation of substances. In many instances, studies on wall materials rely on empirical results with trial-and-error strategies, while focussing mainly on the encapsulation of model biocompounds and the determination of underlying parameters (e.g., encapsulation efficiency, microcapsules stability). However, stability issues of materials intended for microencapsulation purposes are rarely considered.

Rheological and thermal characteristics of the wall materials can be assessed before establishing their potential use as raw materials for encapsulation of biocompounds. The thermal properties commonly studied are glass transition temperature and activation energy. Activation energy (E_a) is a thermal property that can be used as a criterion for establishing the suitability of polymers as wall materials for microencapsulation by spray-drying (Anandharamakrishnan & Ishwarya, 2015). High activation energy ($\sim$25.0–30.0 $kJ{\cdot}mol^{-1}$) of wall materials is desirable to obtain an effective protection of the core during spray-drying (Pérez-Alonso, Báez-González, Beristain, Vernon-Carter, & Vizcarra-Mendoza, 2003). The activation energy can be

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https://doi.org/10.1016/j.foodchem.2018.03.130
Received 18 December 2017; Received in revised form 19 March 2018; Accepted 28 March 2018
Available online 29 March 2018
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determined from the effective diffusional rate and its change with temperature. The water diffusion coefficient for the spray-drying process has been related to the morphology of particles. The effective diffusion coefficient is related to spray-drying kinetics and the diffusional release of encapsulated biocompounds. The diffusion in a porous solid has been attributed to the spreading pressure (Babbitt, 1950). Spreading pressure has been linked to the free surface energy of adsorption, but also to differences in surface tension between void sorption sites in the porous structure and sites filled with water molecules (Al-Muhtaseb, McMinn, & Magee, 2004). Other thermodynamic functions, such as Gibb's free energy, isosteric heat, enthalpy-entropy compensation, differential and integral enthalpy and entropy, reflect the microstructural arrangement of the starch spherical aggregates and their interaction with water molecules (Iglesias, Chirife, & Viollaz, 1976; Pérez-Alonso, Beristain, Lobato-Calleros, Rodríguez-Huezo, & Vernon-Carter, 2006; Velázquez-Gutiérrez et al., 2015). Interestingly, water adsorption isotherms can be used for estimating thermodynamic properties related to heat-moisture stability of wall materials (Beristain, Azuara, & Vernon-Carter, 2002; Spada, Noreña, Marczak, & Tessaro, 2013; Tolstoguzov, 2003). In turn, these properties can be used for establishing optimal storage conditions (moisture and temperature) and protective characteristics (diffusional coefficient and activation energy) (Bonilla, Azuara, Beristain, & Vernon-Carter, 2010).

Most studies on microencapsulation of active compounds are based on empirical tests, commonly derived from trial-and-error methods. The main drawback of empirical approaches is that the results can rarely be extended to general structures, while their derivation may require a large set of experimental runs. The characterization of the thermodynamical properties can provide a systematic way for obtaining *a priori* systematic information on the viability of materials for encapsulation purposes (Beristain et al., 2002). In this regard, the aim of this work was to characterize the thermodynamic properties of taro starch spherical aggregates from adsorption isotherms oriented to assess the viability of this structure for microencapsulation purposes. Specifically, adsorption isotherms were the departing point for estimation of a set of thermodynamic properties linked to valuable information on the thermal stability of spherical aggregates from taro starch.

2. Materials and methods

2.1. Materials

Taro (*Colocassia esculenta* var. Eculenta) corms were harvested in March 2015, in a commercial crop at Veracruz, Mexico. Taro starch was obtained by means of the method and isolation conditions reported by Agama-Acevedo et al. (2011). Taro starch granules exhibited a combination of polygonal and irregular shapes ranging in size from 0.5 to 7.6 μm, protein content of 3.7 ± 0.1 g·100 g^{-1}, amylose content of 12.9 ± 0.8 g·100 g^{-1}. A-type XRD pattern with crystallinity level of 21.5% was obtained for taro starch granules (Hoyos-Leyva, Bello-Pérez, Yee-Madeira, Rodriguez-Garcia, & Aguirre-Cruz, 2017). Also, amylose and amylopectin fractions had weight-average molar masses of 4.3×10^7 g·mol^{-1} and 1.3×10^9 g·mol^{-1}, respectively, and gyration radius (Rz) of 291 and 410 nm, respectively (Hoyos-Leyva, Bello-Pérez, Alvarez-Ramirez, & Agama-Acevedo, 2017).

2.2. Sample preparation

Taro starch spherical aggregates were obtained in a Mini Spray Dryer (Model B-290, BÜCHI UK Ltd, Chadderton, UK) by means of the method reported by Gonzalez-Soto et al. (2011). The inlet and outlet temperature were 145 °C and 80 °C, respectively; while the flow rate was 7.6 g·min^{-1}. Samples were stored in a hermetic glass container for analysis.

2.3. Sorption isotherms

The water adsorption isotherms for all samples were measured via the methodology proposed by Hoyos-Leyva, Agama-Acevedo, Bello-Perez, Vernon-Carter, and Alvarez-Ramirez (2016). To this end, an automated gravimetric water vapour sorption analyser DVS-1 (Quantachrome Instruments, Florida, U.S.A.) was used to analyze the spray-dried starch spherical aggregates. The samples (25.0 ± 1.0 mg) were weighed directly in a sample holder and placed within the weighing chamber. Measurements of adsorption isotherms were conducted at temperature and moisture ranges from 20 to 45 °C and 10 to 90 g $H_2O.g^{-1}$ dry solids of water activity, respectively. The percentage of mass change was considered to calculate the moisture content (g $H_2O.g^{-1}$ dry solids).

2.4. Guggenheim, Anderson and de Boer (GAB) parameters

The well-known GAB model is commonly considered for describing adsorption isotherms for moisture content (Maroulis, Tsami, Marinos-Kouris, & Saravacos, 1988). An important feature of the GAB model is its accountability of multilayer formation on homogeneous surfaces. The GAB equation is considered as an extension of the two-parameter Brunauer-Emmett-Teller (BET) model for adsorption, which takes into account property modifications of the adsorbate in the multilayer region and bulk water (i.e., free water). The GAB model is normally described as follows:

$$M = \frac{M_m C K a_w}{(1-Ka_w)(1-Ka_w + CKa_w)} \quad (1)$$

where the symbol M denotes the moisture content (g $H_2O.g^{-1}$ dry solids), a_w is the water activity and M_m is the moisture content corresponding to an adsorbed monolayer. On the other hand, the parameter C is the so-called Guggenheim constant that corresponds with the heat of sorption, while the parameter K is a correction factor (also called ratio of partition) for interactions between bulk liquid and adsorbed molecules in the multilayer. It should be mentioned that the BET equation can be obtained from the GAB equation when $K = 1$.

2.5. Isosteric heat or differential enthalpy

The isosteric heat of sorption or differential enthalpy is a thermodynamic parameter to obtain valuable information on binding energy between binding sites and water molecules. The isosteric heat of adsorption satisfies the equality $\Delta H_{is} = Q_{st} - \Delta H_{vap}$, where Q_{st} and ΔH_{vap} are the energy required to remove water from the binding sites and the vapourization enthalpy of normal water, respectively. The isosteric heat of sorption was estimated from the adsorptions isotherms via the so-called Clausius-Clapeyron equation (Cadden, 1988):

$$\Delta H_{is} = -R\left(\frac{\partial \ln(a_w)}{\partial \ln(T)}\right)_M \quad (2)$$

To this end, the isosteric heat can be estimated as

$$\Delta H_{is} \approx R\frac{T_1 T_2}{T_1 + T_2}\ln\left(\frac{a_{w,1}}{a_{w,2}}\right) \quad (3)$$

where the computations are carried out for the given two equilibrium states (T_1,$a_{w,1}$) and (T_2,$a_{w,2}$). On the other hand, the free energy, ΔG, of water adsorption in starch spherical aggregates was determined by means of the Gibb's equation:

$$\Delta G = RT\ln(a_w) \quad (4)$$

Also, the total heat of sorption is given by

$$\Delta H = \Delta H_{is} + \Delta H_{vap} \quad (5)$$

Here, ΔH_{vap} is the latent heat of vapourization of free water.

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