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The use of arabic gum, maltodextrin and surfactants in the microencapsulation of phytosterols by spray drying

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ABSTRACT

The addition of phytosterols in aqueous-based food matrices is challenging because of their poor physicochemical properties (non-water soluble and hydrophobic powder). By using spray drying, phytosterols microparticles were formulated and developed in this work. Arabic gum, maltodextrin and one of two different surfactants were thoroughly studied as wall materials. Increasing concentrations of Tween 20 (T20) or sodium lauryl sulfate (SDS), from 0.1 to 2.65% w/v, were evaluated. The feed suspension characteristics (viscosity, interfacial properties and particle size distribution), process yield (PY), encapsulation efficiency (EE), phytosterols retention (R) and size of the microparticles were analyzed. The presence of surfactants in the suspension to be spray dried has significant effects on the studied responses. T20 led to process yields around 65% (2% w/v surfactant concentration). On the other hand, the microparticles obtained using 2% w/v of SDS were the best in terms of EE (about 50%), R (close to 40%) and particle size (5.89 μm), being the PY acceptable (almost 55%). According to the open literature, which indicates that average particle sizes lower than 25 μm favor the phytosterols bioavailability, the microparticles obtained in this work are promising for phytosterols delivery.

1. Introduction

Phytosterols (PS) are vegetable sterols with a similar structure to cholesterol, which cannot be absorbed into the blood stream but are widely recognized as lowering absorption of cholesterol and their serum levels [1]. It has been found that PS exert their hypocholesterolemic effect if they are dispersed [2]. Indeed, the PS must be administered finely divided in order to facilitate their exposure to the bile salts, and preferably in particles smaller than 50 μm to reduce the sandy mouth feel [3]. Furthermore, it has been demonstrated that average particle sizes about 25 μm favor the incorporation of PS into the micellar phase in the intestine improving the bioavailability [2].

Phytosterols and their derivates (stanols, esters and stanol-esters) have been included in fat- or oil-based foods products, which are clearly restricted in diets for hypercholesterolemia [3]. Therefore, the incorporation of PS in aqueous-based formulations (like beverages, soups and others) is an attractive field of application. The hydrophobic and water insoluble nature of PS, which make them poor candidates for stable dispersions, hinder their applicability on intermediate or final aqueous-based products [4].

Several authors focused on particle size reduction to improve the phytosterols dispersibility. Among others, the following techniques have been investigated: a) dry milling of cooled material (e.g., in air mill, air attrition mill, high energy hammer mill, impact mill [2,5]); b) high pressure homogenization of mixtures or dispersions including emulsifiers [6–8]; and c) high pressure homogenization or shearing of melted material [6,9,10]. However, all these techniques are complex and time- and energy-consuming because they require more than one step (homogenization or milling, including cooling or heating) to obtain the desired particle size. Furthermore, for solid phytosterols, several abrasive effects of the homogenizer valves or parts of the milling equipment have been found [6,9,11].

Microencapsulation is a common technique used to provide a physical barrier between the active ingredient and the other components of the product [12]. Among other methods, *spray drying* and *spray chilling* have been successfully applied for encapsulation of food ingredients because it allows producing particles of high quality and stability by means of relatively flexible, simple, low-cost and continuous processes [13,14]. Spray drying consists in the atomization of a solution or liquid suspension into tiny drops, followed by drying in a stream of hot air to produce solid microparticles [15]. On the other hand, spray chilling involves the atomization of a hot melt fluid (solution or suspension) into a cooled chamber to obtain the solid product [16].

To the best of our knowledge, only Alvim et al. [17] studied the microencapsulation of phytosterols by spray chilling using a lipid mixture

Abbreviations: PS, phytosterols; AG, arabic gum; MD, maltodextrin; HLB, hydrophilic–lipophilic balance; SDS, sodium lauryl sulfate; T20, polysorbate Tween 20; PSD, particle size distribution; PY, process yield [%]; EE, encapsulation efficiency [%]; TP, total content of phytosterols [%]; FP, free phytosterols [%]; R, phytosterols retention [%]; D[3,2], Sauter mean [μm]; DSC, differential scanning calorimetry; XRD, X-ray diffraction.

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of low trans-hydrogenated vegetable fat and stearic acid as wall material. The authors analyzed the effect of the ratio of the wall components on the particle size (between 13.8 and 32.2 μm) and morphology. Non data of the process yield, encapsulation efficiency, feed properties and additional product features were reported. Moreover, the wall includes a fatty and trans-material, being not adequate to produce water-dispersible microparticles.

Regarding the microencapsulation of PS by spray drying, very few publications are available in the open literature (i.e., just two patents [3,4]). Auweter et al. [4] proposed the dissolution of PS in an organic solvent (like acetone), followed by the dispersion of the mixture into an aqueous matrix of Na-caseinate and modified starch. After solvent removal, the dispersion was spray dried to obtain a powder product. The mayor disadvantage of this proposal is the use of solvents, which negatively affect the product healthiness and production costs (i.e., a solvent removal step is required). On the other hand, Auriou [3] proposed the creation of micelles comprising PS and surfactants with HLB between 8 and 18 (as sucro-ester) in an aqueous medium, followed by coating of the micelles with starches (a mixture of octenylsuccionate and corn starch) in a spray-drying step, leading to particle sizes between 10–100 μm.

Although these contributions are interesting, none of them covers completely the rational design of a particulate system containing PS with adequate bioavailability and consumer acceptability (particle size lower than 25 μm) by organic solvent free-microencapsulation via spray drying. In fact, the relationships between operating variables, feed composition, process performance and product quality have not been studied. It is well-known that feed formulation is one of the key steps in microencapsulation by spray drying [12].

Mixtures of arabic gum and maltodextrin have been broadly used as wall materials in the microencapsulation by spray drying of many food ingredients [12]. However, no evidences of the use of this mixture for encapsulation of insoluble and waxy solids have been found. Moreover, the research field of microencapsulation of non-water soluble solids has not been widely explored.

Phytosterols processing by spray drying requires stabilized feed emulsions or suspensions. Emulsification implies the use of high temperatures (above the PS melting point, i.e., ≈136 °C) [9,18] or esterified PS (which have lower melting points) [19–21]. However, high temperatures could negatively affect the PS oxidative stability while esterified PS need to be hydrolyzed in order to inhibit cholesterol absorption [22]. On the other hand, the stabilization of aqueous suspensions can be achieved by adding surfactants [23]. Indeed, the use of surfactants in spray drying has proved positive effects; among others, improved stability of the dispersions to be spray dried and, thus, increased encapsulation efficiency [24]. Furthermore, the addition of surfactants tends to diminish the surface tension of the continuous phase, promoting particle disaggregation in the disperse phase [25].

In this context, the aim of this work is to rationally study the microencapsulation of phytosterols using a mixture of arabic gum and maltodextrin as wall materials. Particularly, the effect of the addition of two different surfactants, nonionic (Tween 20) or anionic (Sodium lauryl sulfate), on the process yield, encapsulation efficiency, phytosterols retention and product particle size is evaluated. Complementarily, important parameters of the feed formulation are analyzed: wetting of phytosterols by the wall solutions (containing the wall materials and the surfactant), viscosity of the feed suspensions and size of the particles in these feed suspensions.

2. Materials and methods

2.1. Materials

Phytosterols powder and arabic gum were supplied by Grupo Saporiti (Buenos Aires, Argentina). The PS powder consisted in a mixture of β-sitosterol (35–55% w/w), campesterol (18–27% w/w), stigmasterol (21–35% w/w) and about of 0–7% w/w of other vegetable sterols. According to X-ray diffraction (XRD) and differential scanning calorimetry (DSC) measurements previously performed, pure phytosterols present a crystalline structure and a melting point around 136 °C (see Supplementary data, Figures S1 and S2, respectively). The particle size distribution of raw material was measured by laser diffraction (see Section 2.2.2.3), being the Sauter mean 46.4 ± 1.1 μm.

Maltodextrin Globe® 019150 (dextrose equivalent, DE 15) was supplied by Todo Droga (Córdoba, Argentina). The phytosterols, arabic gum (AG) and maltodextrin (MD) were food grade. The pro-analysis grade surfactants, sodium lauryl sulfate (SDS) (HLB 40, molecular weight 289) and polysorbate Tween 20 (T20) (HLB 16, molecular weight 1228) were supplied by Cicarelli® Reagents S.A. (Santa Fe, Argentina).

2.2. Methods

2.2.1. Liquid feed preparation

The liquid feed to the spray dryer was prepared by dissolution of the wall materials and the surfactant in distilled water, followed by dispersion of the PS powder and homogenization. Table 1 shows the *feed suspensions* composition for all the studied cases: reference feed (*FR*, without surfactant), feeds comprising T20 in different concentrations (*FT1* to *FT6*) and feeds containing SDS in different concentrations (*FS1* to *FS6*).

Briefly, 15 g of arabic gum and 5 g of maltodextrin were dispersed in 100 mL of hot distilled water (50 °C) under magnetic stirring, until complete dissolution and hydration (about 30 min). Then, the surfactant (SDS or T20) was added to form the *wall solutions* (Table 1). Finally, 6.66 g of PS were dispersed under continuous agitation for 1 h. Afterward, the aqueous suspensions to be spray dried were homogenized using a Pro II Homogenizer over 9 min at 25,000–35,000 rpm and room temperature. These conditions and the AG, MD and PS contents in the suspensions were selected based on previous exploratory experiments.

2.2.2. Liquid feed characterization

2.2.2.1. Contact angle between phytosterols and wall solutions. For each wall solution (aqueous solution of AG, MD and surfactant; see Table 1) the contact angle on phytosterols was determined by the sessile drop method; i.e., by tangential observation of a tiny solution droplet (20 μL) that was placed over a glass plate, which was previously coated with a thin layer of phytosterols. The phytosterols layer was prepared by dissolution of PS powder in hexane, followed by deposition of this solution on the entire surface of the glass plate. The high volatility of hexane facilitated the formation of a thin and uniform solid PS layer. The wetting experiments were performed at room temperature in a Krüss DSA Mk2 goniometer equipped with image analysis software (Drop Shape Analysis, Krüss GmbH, Germany). The contact angle was measured at the initial state (t = 0 min) and 5 min after the drop deposition. The assays were performed in duplicate.

2.2.2.2. Viscosity of the feed suspensions. The viscosity of the suspensions was determined with a controlled-stress rheometer Physica MCR 301 Anton Paar (Ostfildem, Germany) at room temperature and shear rates from 0 to 1000 s^{-1}. A coaxial-cylinder geometry (CC27-SN16635) was used. The viscosity was calculated from the steady-shear flow curves, as the ratio between shear stress and shear rate. All measurements were performed in duplicate.

2.2.2.3. Particle size distribution of the feed suspensions. The particle size distribution (PSD) of the homogenized suspensions was measured by laser light diffraction using a Horiba LA-950 V2 device (Irvine, United States). Average particle size was expressed as D[3,2], i.e., the Sauter

Table 1
Composition of the wall solutions and feed suspensions (wall solutions plus PS), and properties of the feed suspensions and microparticles.

Wall solution	AG [% w/v]	MD [% w/v]	Surfactant* [% w/v]	Feed suspension	PS [% w/v]	Viscosity** [mPa · s]	D[3,2]** [μm]	Microparticle	D[3,2]** [μm]
WR (*reference*)	15.00	5.00	0.00	*FR* (*reference*)	6.66	18.94 ± 0.40^{c}	14.7 ± 0.8^{d}	*MR* (*reference*)	8.9 ± 0.3^{d}
WT1	15.00	5.00	0.10	*FT1*	6.66	20.02 ± 0.16^{d}	16.3 ± 0.93^{e}	*MT1*	8.9 ± 0.1^{d}
WT2	15.00	5.00	0.50	*FT2*	6.66	15.11 ± 0.04^{a}	$13.53 \pm 0.6^{b,c}$	*MT2*	$7.5 \pm 0.5^{a,b}$
WT3	15.00	5.00	1.00	*FT3*	6.66	14.84 ± 0.17^{a}	$14.0 \pm 0.2^{c,d}$	*MT3*	$7.9 \pm 0.0^{b,c}$
WT4	15.00	5.00	1.50	*FT4*	6.66	18.77 ± 0.39^{c}	$12.4 \pm 0.5^{a,b}$	*MT4*	$7.4 \pm 0.5^{a,b}$
WT5	15.00	5.00	2.00	*FT5*	6.66	17.21 ± 0.16^{b}	11.3 ± 0.7^{a}	*MT5*	6.8 ± 0.1^{a}
WT6	15.00	5.00	2.65	*FT6*	6.66	16.83 ± 0.22^{b}	12.6 ± 0.6^{b}	*MT6*	$8.4 \pm 0.1^{c,d}$
WS1	15.00	5.00	0.10	*FS1*	6.66	22.67 ± 0.31^{B}	13.1 ± 0.1^{D}	*MS1*	8.2 ± 1.6^{A}
WS2	15.00	5.00	0.50	*FS2*	6.66	16.04 ± 0.41^{A}	9.4 ± 0.9^{C}	*MS2*	6.1 ± 0.6^{B}
WS3	15.00	5.00	1.00	*FS3*	6.66	22.44 ± 0.55^{B}	$7.9 \pm 0.4^{B,C}$	*MS3*	5.8 ± 0.1^{B}
WS4	15.00	5.00	1.50	*FS4*	6.66	32.62 ± 2.27^{C}	$6.8 \pm 1.8^{A,B}$	*MS4*	5.5 ± 0.3^{B}
WS5	15.00	5.00	2.00	*FS5*	6.66	31.49 ± 1.96^{C}	5.6 ± 1.2^{A}	*MS5*	5.9 ± 0.1^{B}
WS6	15.00	5.00	2.65	*FS6*	6.66	41.30 ± 1.44^{D}	5.1 ± 0.6^{A}	*MS6*	5.8 ± 0.4^{B}

* WT1 to WT6, FT1 to FT6 and MT1 to MT6: Surfactant = T20; and WS1 to WS6, FS1 to FS6 and MS1 to MS6: Surfactant = SDS.
** For each column and surfactant, different letters indicate significant differences ($p < 0.05$).

mean or surface–volume mean (i.e., the mean size that conserves the surface and volume of the original population). The refractive index used for statistical calculation of the particle size was 1.358. Three repetitions were conducted for each sample.

2.2.3. Spray-drying operating conditions

The suspensions were spray dried in a co-current Mini Spray Dryer Büchi B-290 (Büchi Labortechnik AG, Flawil, Switzerland), provided with a two-fluid nozzle with a cap orifice diameter of 0.5 mm. During atomization, the suspensions were kept agitated by means of a magnetic stirrer bar at 800 rpm, approximately. The operating conditions were: drying air inlet temperature: 160 °C, atomization air volumetric flowrate: 601 L/h, feed volumetric flowrate: 2 mL/min and drying air volumetric flowrate: 35–38 m^3/h. These conditions were selected based on previous exploratory experiments. All the assays were performed in duplicate. The outlet temperature was always below 102 °C. Immediately after the spray-drying step, the microparticles water content was determined by using a moisture analyzer with halogen heating (model M45, OHAUS). Sample moisture content analysis was performed at 105 °C until constant weight. For all the studied samples, the water content was in the range 3 to 5% w/w. Besides, XRD and DSC measurements were carried out. The microparticles diffractograms showed the PS characteristic peaks, indicating that the crystalline structure of phytosterols is not significantly affected (Figure S3 in Supplementary data). On the other hand and according to the DSC thermograms, no evidence of glass transition temperature was found for the product microparticles (Figure S4 in Supplementary data). Considering the crystalline state of PS in the microparticles and their low water content, good powder stability is expected.

2.2.4. Product particle size distribution and morphology

The product particle size distribution was also measured by laser light diffraction (wet mode) using a Horiba LA-950 V2 device (Irvine, United States). D[3,2] was considered as the average particle size of the microparticles. Three repetitions were conducted for each sample.

Particle morphology was assessed using an EVO 40-XVP, LEO Scanning Electron Microscope (SEM) (Oberkochen, Germany). Previously, the obtained powders were dried under air flow on a porthole and metalized with gold in a PELCO 91000 sputter coater (Tedpella, United States).

2.2.5. Process yield

The process yield (PY) was determined gravimetrically as the ratio of the amount of powder collected after every spray-drying experiment to the initial amount of solids contained in the feed suspensions (see Eq. (1)).

$$PY[\%] = \frac{\text{Mass of Powder Collected}}{\text{Mass of Solids Fed}} \cdot 100\% \quad (1)$$

2.2.6. Encapsulation efficiency

The encapsulation efficiency (EE) is defined by Eq. (2) as the ratio between the encapsulated and total phytosterols in the spray-dried product:

$$EE[\%] = \frac{TP\text{-}FP}{TP} = \frac{\text{Mass of Encapsulated Phytosterols}}{\text{Mass of Total Phytosterols Collected}} \cdot 100\% \quad (2)$$

where TP and FP are the amount of total and free (non-encapsulated) phytosterols in the microparticles, respectively. Both TP and FP were determined by solvent extraction, following the methodology described by Velasco et al. [26] (see Subsections 2.2.6.1 and 2.2.6.2).

2.2.6.1. Total content of phytosterols. The experimental procedure was based on the Rose–Gottlieb method, which is widely accepted for quantitative determination of fat in milk and milk powders. A quantity of 4 g of microparticles was dispersed in 40 mL of distilled water heated at 65 °C. After stirring gently, 8 mL of 25% NH_4OH were added and the suspension was heated at 65 °C for 20 min in a shaking water bath. Then, the suspension was cooled at room temperature and the lipids were extracted in a separatory funnel applying three liquid–liquid extractions: first, 20 mL of ethanol, 50 mL of ethyl ether and 50 mL of n-hexane; second, 10 mL of ethanol, 50 mL of ethyl ether and 50 mL of n-hexane; and, third, 50 mL of ethyl ether and 50 mL of n-hexane. In each extraction step, the solvents were added successively with shaking between additions. The upper phase was collected and filtered through a filter paper containing anhydrous Na_2SO_4, and then evaporated and dried to constant weight under nitrogen stream. The total content of phytosterols (TP) was expressed as:

$$TP[\%] = \frac{\text{Mass of Total Phytosterols Collected}}{\text{Mass of Total Solids Collected}} \cdot 100\%. \quad (3)$$

2.2.6.2. Free content of phytosterols. The free phytosterols fraction was extracted by stirring 5 g of microparticles in a volume of 200 mL of n-hexane, during 15 min at room temperature. After filtration through a filter paper, the solvent was evaporated in a rotary evaporator (at 60 °C and 0.200 kg/cm^2 approximately) and the extracted phytosterols

were dried to constant weight under nitrogen stream. The free content of phytosterols (FP) was expressed as:

$$FP[\%] = \frac{\text{Mass of Free Phytosterols Collected}}{\text{Mass of Total Solids Collected}} \cdot 100\%. \quad (4)$$

2.2.7. Phytosterols retention

The phytosterols retention (R) is the ratio between the amount of total phytosterols in the spray-dried product (encapsulated and free) and the amount of phytosterols fed in the aqueous suspension.

$$R[\%] = \frac{\text{Mass of Total Phytosterols Collected}}{\text{Mass of Total Phytosterols Fed}} \cdot 100\% \quad (5)$$

2.2.8. Statistical analysis

The statistical evaluation of the results was carried out by analysis of variance (ANOVA). Statistical significance was established through p-value; values lower than 0.05 indicate that the factor impact is significant with at least 95% confidence.

3. Results and discussions

3.1. Wettability of wall solutions on phytosterols

Wettability describes the ability of a solid surface to be wetted by a liquid and, thus, the potential of the liquid continuous phase to stabilize and encapsulate the dispersed phase. It is generally characterized in terms of the contact angle, i.e., the angle formed by the intersection of the liquid/solid interface and the liquid/vapor interface (geometrically acquired by applying a tangent line from the contact point along the liquid/vapor interface in the droplet profile) [27]. A contact angle less than 90° indicates that wetting of the surface is favorable, and the liquid will spread over a large area on the surface; while contact angles greater than 90° generally mean that wetting of the surface is unfavorable so the liquid will minimize its contact with the surface and form a compact liquid droplet [28,29].

Fig. 1 shows the variation of the contact angle with the surfactant concentration at the initial state (t = 0), for the wall solutions containing T20 or SDS (the results corresponding to t = 5 min are presented in the Supplementary data, Figure S5). As it can be seen, the contact angle is significantly affected by the addition of surfactants ($p < 0.05$). Additionally, Fig. 1 includes the images of the sessile droplet experiment, for the wall solutions *WR*, *WT1* to *WT6* and *WS1* to *WS6*, immediately after the drop deposition on the phytosterols layer. In the absence of surfactants (*WR*), the drop appears turgid and almost spherical due to the hydrophobic nature of PS. Poor wetting is observed despite the surface activity provided by AG [30]. Surfactants greatly enhanced the wetting, being the PS layer best wetted by the wall solution *WS6* (i.e., 2.65% w/v of SDS). In fact, after the impact on the PS layer, this liquid drop spread out the most on the powder surface.

For the wall solutions including T20, the contact angle decreases from 124° to almost 90° when the surfactant concentration rises from 0 to 0.5% w/v (*WR* to *WT2*). For higher T20 concentrations, the contact angle remains almost constant and close to the wetting boundary. This trend is in agreement with results reported by Wang et al. [31] for a system comprising hydrogenated soybean oil (solid phase) and T20 aqueous solutions. The observed contact angle behavior, together with surface tension measurements previously performed for the wall solutions (*WR* and *WT1* to *WT6*) and feed suspensions (*FR* and *FT1* to *FT6*) (see Figure S6, in Supplementary data), suggest that the liquid/air interface would be saturated with the surfactant for the studied T20 concentration range [32].

For the wall solutions based on SDS (*WS1* to *WS6*), the contact angle decreases as the SDS concentration increases over the whole studied range. Above 1.5% w/v of SDS (*WS4*), the wall solutions become good wetting liquids (i.e., contact angle <90°), being the contact angle about 50° for the wall solution *WS6* (2.65% w/v of SDS).

Therefore, both surfactants significantly improve the interaction between the wall materials and phytosterols ($p < 0.01$). Moreover, SDS provides lower contact angles than T20, probably due to the difference

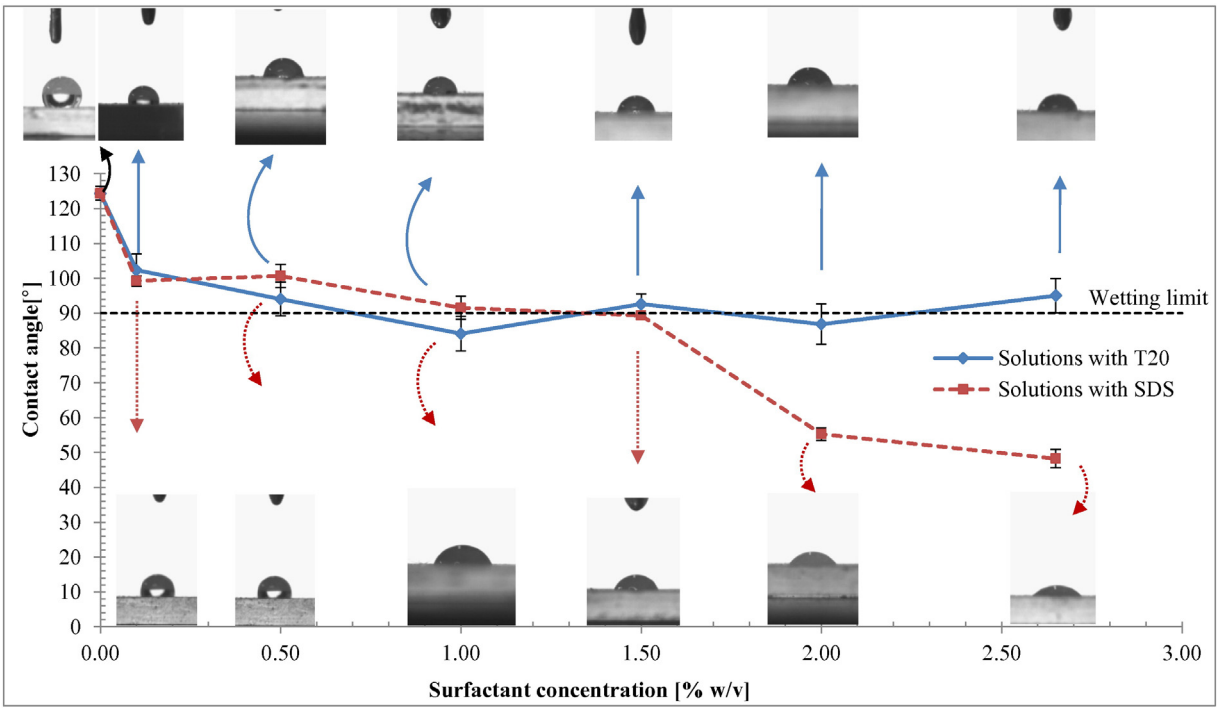

Fig. 1. Contact angle between phytosterols and wall solutions as a function of the surfactant concentration.

in surface tension [33,34] and in the hydrophilic–lipophilic balance [23,35]. In fact, Yılmaz et al. [36] observed a decrease in the contact angle of sunflower oil on compression molded starch samples with an increase in the HLB of the surfactant. The surface tension measurements previously performed (in order to explore the effect of the surfactant type and concentration on the equilibrium surface activity of the wall solutions and feed suspensions) indicated that the surface tension of the formulations comprising SDS (*WS1* to *WS6* and *FS1* to *FS6*) is about 25–30% lower than those corresponding to the formulations including T20 (*WT1* to *WT6* and *FT1* to *FT6*) (see Figure S6, in Supplementary data).

3.2. Viscosity of the feed suspensions

According to technical data provided for the Mini Spray Dryer Büchi B-290, the viscosity of the liquid feeds to be spray dried should be lower than 300 mPa.s to ensure good atomization (www.büchi.com). Besides, it has been reported that the feed viscosity has significant effects on microencapsulation by spray-drying [12,37,38]. For these reasons, the rheological behavior of the feed aqueous suspensions was investigated.

Fig. 2 shows the variation of the viscosity with the shear rate for the feed suspensions without surfactant (*FR*) and with 2% w/v of T20 and SDS (*FT5* and *FS5*, respectively), as representative examples of the viscosity-shear rate dependence. The results corresponding to the other studied samples (*FT1* to *FT4* and *FT6*, *FS1* to *FS4* and *FS6*) are presented in the Supplementary data (Figure S8). As the viscosity remains almost constant within the shear-rates studied range, the Newtonian model gives a good description of the experimental data [39]. These results could be attributed to the presence of arabic gum as the main component, which rheological behavior is Newtonian. Tonon et al. [40] and Frascareli et al. [41] observed similar trends for linseed and arabic gum emulsions, and in the microencapsulation of coffee oil with arabic gum as wall material, respectively.

Table 1 also presents the viscosity obtained by fitting the experimental data to a Newtonian model. The R^2 coefficient is above 0.999 in all cases. For both surfactants, its addition and concentration significantly affect the viscosity ($p < 0.05$). For the feed suspensions comprising T20, the viscosity is between 15 and 20 mPa.s; while for the feed suspensions based on SDS, the viscosity is between 16 and 41 mPa.s. All the feed suspension viscosity values are considerable lower than the maximum admissible viscosity, guaranteeing their processing by spray drying.

Although some fluctuations are observed (possibly due to foam formation [42]), the viscosity of the feed suspensions including SDS tends to increase with the surfactant concentration (*FS1* to *FS6*). This can be attributed to the higher dissolved solid content [41], the smaller mean particle size and the narrower PSD (see next section) [42,43].

3.3. Particle size distribution of the feed suspensions and spray-dried products

The spray-dried particle size (one of the main product quality parameters) and encapsulation efficiency are usually affected by the size of the particles in the feed suspension. The suspension stability (required to homogeneously feed continuous processes) is also strongly related to this property.

The Sauter mean D[3,2] for the feed suspensions and corresponding spray-dried products (microparticles) are also presented in Table 1. D[3,2] significantly depends on the surfactant concentration ($p < 0.05$), for both T20 and SDS. For the suspensions with T20 (*FT1* to *FT6*), D[3,2] is between 11 to 17 μm, close to the Sauter mean of the feed suspension without surfactant (*FR*, D[3,2] ≈ 15 μm). The D[3,2] of the corresponding microparticles (*MT1* to *MT6*) is in the range 6.7–9 μm, around that of the microparticles without surfactant (*MR*, D[3,2] ≈ 9 μm).

On the other hand, for the suspensions and microparticles containing SDS (*FS1* to *FS6* and *MS1* to *MS6*, respectively), an important decrease in D[3,2] is found as the surfactant concentration increases (e.g., from about 13 to 5 μm and 8 to 5 μm, for suspensions and microparticles, respectively). The lower mean particle sizes provided by SDS could be first attributed to the lower contact angles. In effect, and according to Tinke et al. [44], better wetting promotes powder dispersion and breaks apart existing agglomerates. Moreover, a liquid is ideal to disperse powders when it has, among other features, low surface tension [31,44].

Fig. 3a presents the particle size distribution of the raw phytosterols while Fig. 3b, 3c and 3d show the PSD of the suspensions without surfactant (*FR*) and with 2% w/v of T20 or SDS (*FT5* and *FS5* as representative examples of the shape of the PSD curves comprising surfactants), respectively. The results corresponding to the other studied feed suspensions (*FT1* to *FT4* and *FT6*, *FS1* to *FS4* and *FS6*) are given in the Supplementary data (Figure S9). According to these PSDs, less than 8% of the particles population is below 25 μm for the raw phytosterols, while for the feed suspensions *FR*, *FT5* and *FS5* these values are about 35%, 45% and 83%, respectively. These results are in concordance with the viscosity values reported in the previous section.

Generally, the microparticles D[3,2] is lower than the mean size of the particles in suspension ($p < 0.05$). This effect could be explained by the fact that larger particles tend to collide more frequently on the

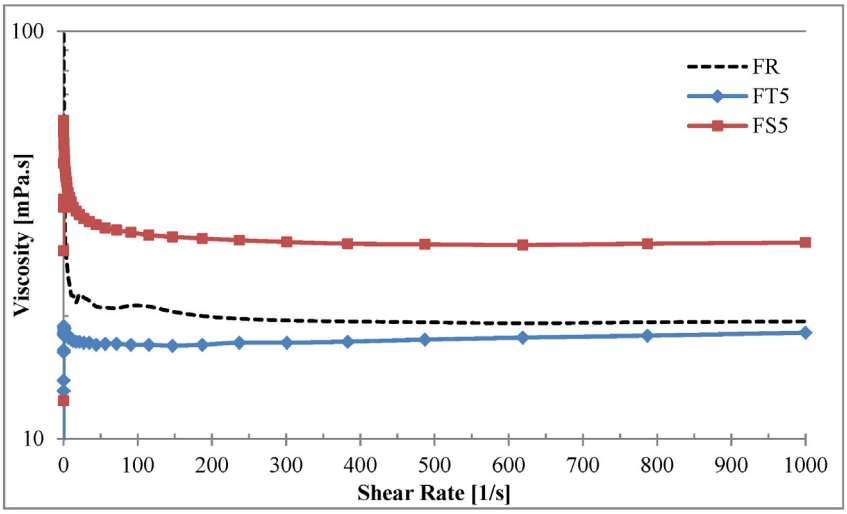

Fig. 2. Rheological behavior of the feed suspensions *FR* (without surfactant), *FT5* and *FS5* (with 2% w/v concentration of T20 and SDS, respectively).

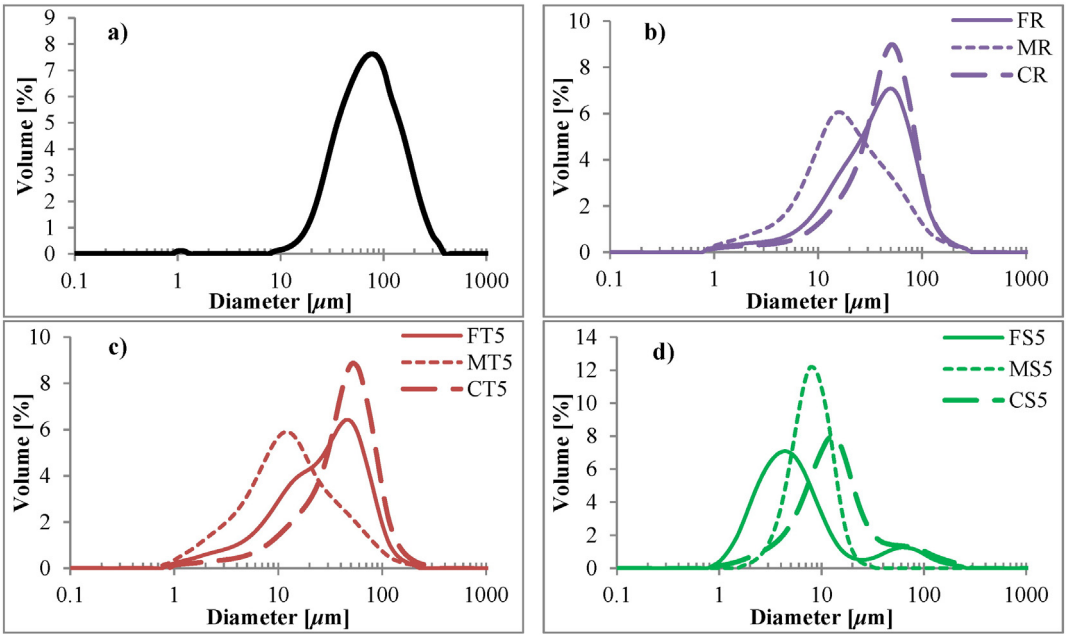

Fig. 3. Particle size distribution of: a) raw phytosterols (PS); b) *FR*, *MR* and *CR* (material stuck on the chamber wall for the reference sample); c) *FT5*, *MT5* and *CT5* (corresponding stuck material); and d) *FS5*, *MS5* and *CS5* (corresponding stuck material).

drying chamber than smaller particles. Indeed, the mean particle size of the material stuck on the spray-dryer wall is usually bigger than that corresponding to the microparticles. This can be seen in Fig. 3b, 3c and 3d, which also include the PSDs for the product microparticles and stuck material for the samples without surfactant (*MR* and *CR*) and with 2% w/v of T20 or SDS (*MT5*, *CT5*, *MS5* and *CS5*), respectively. The results corresponding to the other studied microparticles (*MT1* to *MT4* and *MT6*, *MS1* to *MS4* and *MS6*) are reported in the Supplementary data (Figure S9). For all the obtained spray-dried products, the D[3,2] satisfies the more restricted upper size limit of 25 μm, which is necessary to guarantee the incorporation of PS into the intestine micellar phase [2]. Furthermore, for all the studied microparticles, the measured PSDs are invariant over time, indicating good powder redispersibility. In addition and as it can be seen in Fig. 3b to d, the product PSDs are narrower than the corresponding feed suspension PSDs due to the stickiness of the coarse tail on the wall chamber (in fact, all the raw materials are non-volatile and, thus, cannot be lost by evaporation during the drying process). About 65%, 77% and 98.5% of the microparticles population are below 25 μm for the products without surfactant (*MR*) and with 2% w/v of T20 (*MT5*) and SDS (*MS5*), respectively.

Fig. 4 shows, as an example, the SEM micrographs of the microparticles obtained via spray drying of suspensions *FR*, *FT5* and *FS5* (Fig. 4e, f and g, respectively). For comparative purposes, Fig. 4 also presents the SEM micrographs of each component independently spray dried (except T20 because is liquid at room temperature) at the same operating conditions (Fig. 4a to d).

The microparticles of arabic gum (Fig. 4a) and maltodextrin (Fig. 4b) seem to be deformed and dented spheres with smooth and shriveled surfaces, respectively; being these typical morphologies of polymeric spray-dried powders [40]. On the other hand, the spray-dried SDS microparticles are irregular and considerable smaller (Fig. 4c). Phytosterols particles appear as small partially melted crystals (Fig. 4d), some needle-shaped and others like scales. Türk et al. [45] found similar structures for a phytosterols mixture, which was mainly composed by β-sitosterol, stigmasterol and campesterol.

The reference microparticles (Fig. 4e) are mainly agglomerates constituted by buckled particles while the microparticles obtained by spray drying of the suspensions comprising T20 are mostly agglomerates composed of primary particles with wrinkled structure (Fig. 4f). The observed aggregates are in agreement with the particle size measured by laser diffraction (Fig. 3b and c). On the other hand, the microparticles including SDS are smaller and smoother spheres (Fig. 4g). As it can be seen, the sample is mainly composed by very small particles, in agreement with the PSD shown in Fig. 3d for the microparticles based on SDS (*MS5*). Therefore, the morphology of the microparticles is mainly governed by the nature of the surfactant (see also Figure S10 in Supplementary data, which includes the SEM micrographs corresponding to the microparticles *MT1*, *MT3*, *MS1* and *MS3*). Besides, all the microparticles (i.e., without surfactant or including T20 or SDS) have continuous wall and no apparent fissures or cracks, being these important features to provide better PS protection and retention. Furthermore, their morphologies are clearly different from those corresponding to the pure materials.

3.4. Process yield, encapsulation efficiency and phytosterols retention

Fig. 5 shows the process yield (PY), encapsulation efficiency (EE) and phytosterols retention (R) as a function of the surfactant concentration in the feed suspensions.

As expected, the process yield is significantly affected by the addition of surfactants [33,46], diminishing from 58.24% (in absence of surfactant) to less than 50% when the surfactants are in low proportions. After reaching a minimum value for 0.1% w/v of surfactant, the PY increases with the surfactant concentration ($p < 0.05$). This behavior could be explained in terms of the smaller particle sizes in the feed suspensions. The increase in PY with the surfactant concentration is more marked in the case of T20. In fact, for concentrations higher than 1.5% w/v, the PY overcomes the value obtained for the feed suspension without surfactant (*FR*), ending up at 65%. Regarding the feed suspensions containing SDS, even though the PY increases with the surfactant concentration, it remains below 58.24% (i.e., the process yield of the feed suspension, *FR*, without surfactant).

For all the studied surfactant concentrations, the process yield is higher for the feed suspensions based on T20 (with respect to those comprising SDS) as a consequence of the higher surface tension [33] and lower feed viscosity (see Section 3.2.) [12,47], being both properties commonly associated to product losses by stickiness in spray-drying

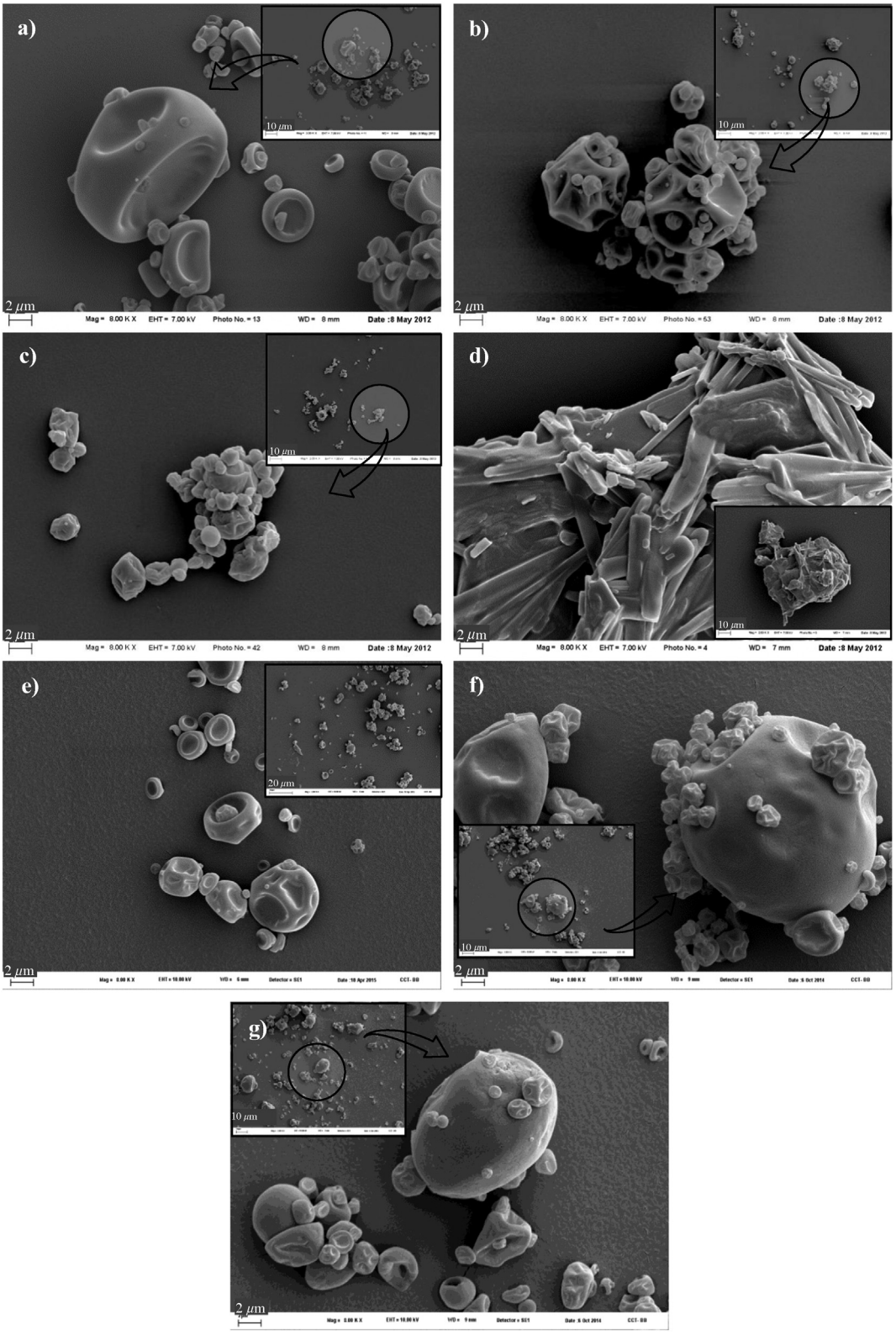

Fig. 4. Scanning electron micrographs of spray-dried microparticles (small and big pictures taken at 2000× and 8000×, respectively): a) Spray-dried AG; b) spray-dried MD; c) spray-dried SDS; d) spray-dried PS; e) microparticles of reference (*MR*); f) microparticles *MT5*; and g) microparticles *MS5*.

chambers [33]. Nevertheless, all the obtained process yields are satisfactory for lab-scale spray-dryers.

The encapsulation efficiency and phytosterols retention are also significantly affected by the surfactant concentration ($p < 0.05$). EE and R decrease from 20 and 22% (feed suspension *FR*, without surfactant) to 10.8 and 18.5% for 0.1% w/v of T20, respectively. For T20 concentrations higher than 0.1% w/v, both EE and R increase with the surfactant concentration up to 23.8 and 32.5%, respectively. On the other hand, EE

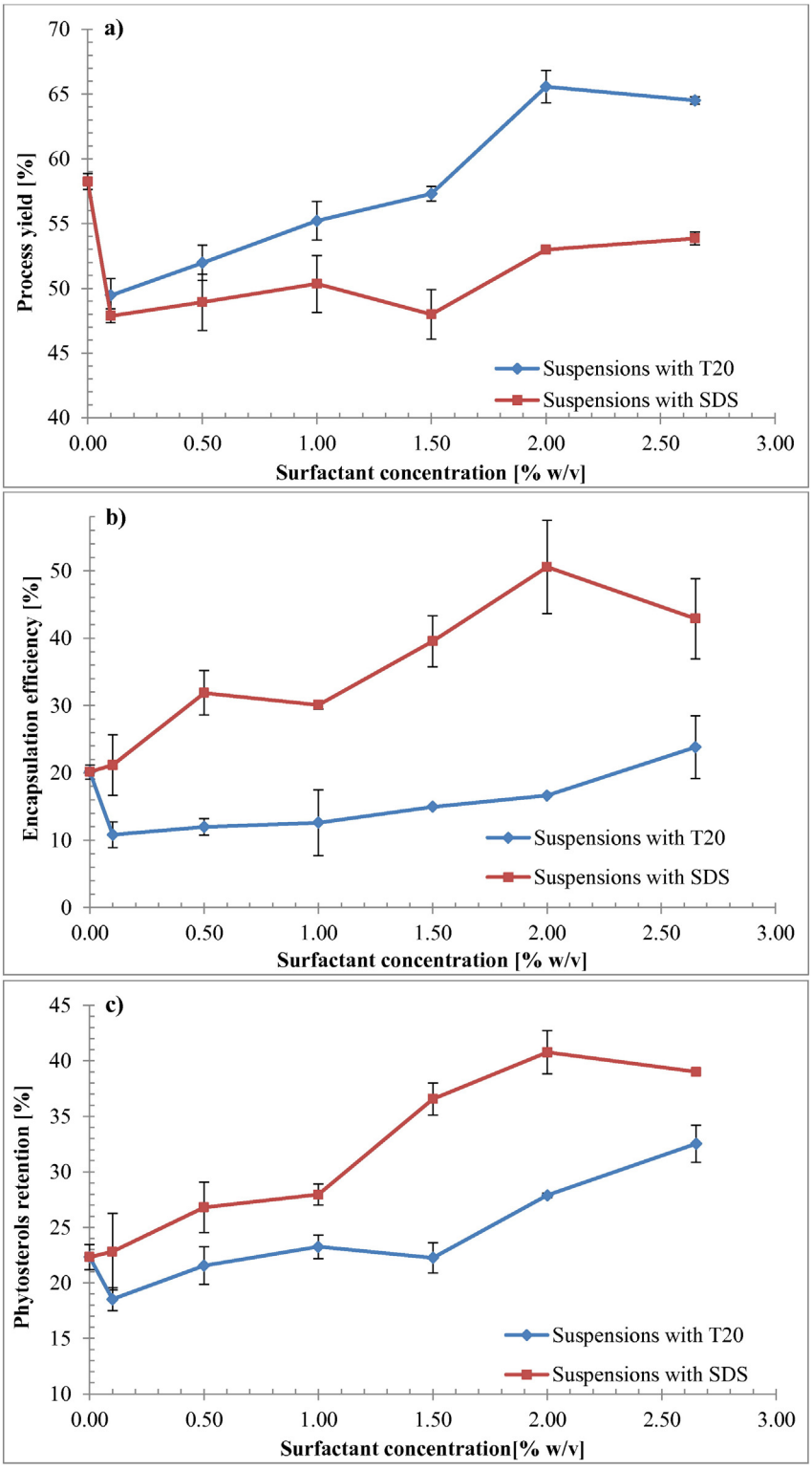

Fig. 5. Influence of surfactant concentration on: a) process yield; b) Encapsulation efficiency; c) Phytosterols retention.

and R increase almost monotonically with the SDS concentration, reaching maximum values of 50.6 and 40.8%, respectively.

For both T20 and SDS, the variations in EE with surfactant concentration are in concordance with the behaviors observed for the contact angle. In fact, the higher encapsulation efficiencies found for the microparticles comprising SDS (with respect to those based on T20) are related to the lower contact angles, which indicated a better interaction between the PS and wall solutions including this surfactant (*WS1* to *WS6*) (see Section 3.1). Besides, the smaller sizes of the particles in the feed suspensions including SDS (Table 1 and Fig. 3d) could be favoring the encapsulation process. Indeed, for the spray drying of O/W emulsions, several authors reported higher EE for smaller emulsion droplet sizes [37,40,41,48].

Despite the lower process yields, phytosterols retention is higher for the microparticles comprising SDS (in comparison to those microparticles based on T20) due to the higher EE. The higher the encapsulation

efficiency, the lower the amount of free PS and, thus, the lower the probability of phytosterols loss by stickiness on the spray-dryer chamber wall.

4. Conclusions

The encapsulation of phytosterols (non-water soluble and hydrophobic solids) by spray drying using a combination of maltodextrin, arabic gum and low concentrations of surfactant (T20 with HLB 16 or SDS with HLB 40) was successfully achieved.

A significant effect of the type and concentration of surfactant on the process yield, encapsulation efficiency, phytosterols retention and product quality was found. All the observed trends were well correlated with studied feed properties (feed suspensions viscosity, particle size of the dispersed phase and wettability of wall solutions on the phytosterols). Although higher process yields were obtained by including T20, the addition of SDS led to better and satisfactory encapsulation efficiency and phytosterols retention, smaller microparticles sizes and adequate process yield for laboratory-scale spray dryers. The enhancement in performance given by SDS (with respect to T20) was explained in terms of the greater affinity between phytosterols and wall solutions. For all feed formulations, the microparticles Sauter mean satisfies the more restricted upper size limit of 25 μm, which is required to ensure the incorporation of phytosterols into the intestine micellar phase.

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