CHITOSAN MICROPARTICULATE SYSTEMS PREPARED BY POLYMER-SURFACTANT INTERACTION

Sandu PERETZ,[a] Manuela FLOREA-SPIROIU,[b,*] Dan F. ANGHEL,[a]
Cristina STOIAN[c] and Gheorghe ZGHEREA[c]

[a] "I. Murgulescu"Institute of Physical Chemistry, Roumanian Academy, Department of Colloids, 202 Spl. Independentei, 060021, Bucharest, Roumania
[b] University of Bucharest, Faculty of Chemistry, Department of Physical Chemistry, 4-12 Regina Elisabeta Blvd., 030018, Bucharest, Roumania
[c] "Dunarea de Jos" University of Galați, Faculty of Sciences and Environment, Department of Chemistry, 111 Domneasca St., 800201 Galați, Roumania

In the current study the synthesis of microparticulate systems through the interaction between chitosan (CHI) and sodium laureth sulfate (SLES) was investigated. Depending on pressure conditions of synthesis two types of particles were prepared: particles at atmospheric pressure, and fine particles at high pressure. At atmospheric pressure, the particles were formed instantaneously when the CHI solution was dripped into the SLES aqueous solution. Depending on the weight ratio between chitosan and surfactant, the polymer-surfactant complex gel may appear as capsules with excrescence, spherical particles or nonspherical particles. To obtain fine particles, the surfactant solution in contact with high pressure CO_2 was sprayed into chitosan solution bath through a stainless steel syringe needle forming the chitosan/surfactant complex. It was found that increasing the spaying pressure leads to lower average diameter of fine CHI-SLES particles, and zeta potential showed that the particles are positively charged. Fourier Transform Infrared Spectroscopy proves the interaction between the sulfate groups of SLES and the amino groups of CHI. The Scanning Electron Microscopy reveals that the fine particles are quasi-spherical, but some of them can take the form of pellets, depending on the preparation conditions.
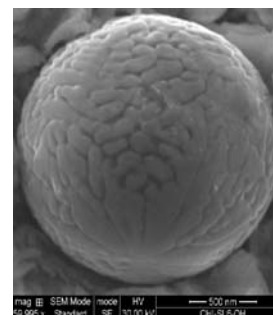
INTRODUCTION

In recent years, the preparation methods of particulate systems have diversified, so interaction between polymers and surfactants became an intensively utilized method to obtain particles due to their special properties, control of particle size and the possibility to use them for multiple applications.

Interactions between polymers and surfactants in aqueous solutions have been the subject of a lot of research, and a number of reviews and papers have been published.[1-3]

The binding isotherms of ionic surfactants by polymers of opposite charge were used to characterize the formation of polymer-surfactant complexes. The complex formation is principally induced by the highly cooperative interaction between ionic polymers and surfactants of opposite charge in dilute solution.[4, 5] To obtain a polymer-surfactant complex in dilute and semi-dilute

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[*] Corresponding author: manu.spiroiu@gmail.com

polymer solutions, the surfactant micellization is the most important process, even if it is influenced by the polymer presence.[6] In the case of hydrophilic polyelectrolytes, the surfactants of opposite charge form micelles and surfactant-polymer attraction is purely electrostatic, therefore ionic micelles are separated from the oppositely charged polyelectrolytes by a layer of water molecules.[7] The surfactants may associate with polyelectrolytes through electrostatic interactions, giving rise to supramolecular aggregates called surfactant polyelectrolyte complexes.[8]

The polymer-surfactant complexes can be present in the system as soluble entities, as particles of colloidal size or gels with good mechanical properties.[9] The interaction between ionic polymers and oppositely charged surfactants is dominated by electrostatic forces, causing the association to start at a very low surfactant concentration, known as the critical aggregation concentration (CAC), usually a few orders of magnitude lower than the critical micelle concentration (CMC) of the surfactant.[10]

In the present study we used sodium laureth sulfate (SLES) as anionic surfactant, which unlike sodium dodecyle sulfate (SDS) possesses ethylene oxide groups (EO) between the hydrophilic moiety and dodecyl hydrophobic group, which increase the overall hydrophobicity of the surfactant. SLES belongs to a class of anionic surfactant which is widely used in shampoos, detergent and other commercial cleaning products. SLES is characterized by the alkyl chain length, the average ethylene oxide content and size distribution of EO domains (narrow). These features drastically affect some physical properties of surfactant such as solubility, viscosity, wetting, foaming, emulsifying, dispersing and cleaning in commercial products.[11]

Biopolymer chitosan is non-toxic, biocompatible and biodegradable willing to form complexes with anionic surfactants. Chitosan, poly(β-1-4)-2-amino-2-deoxy-D-glucopyranose, is produced by partially alkaline N-deacetylation of chitin. Chitin can be widely found in the exoskeleton of shellfish, shrimps, lobsters, as the second most abundant natural biopolymer next to cellulose. The amino and hydroxyl groups of chitosan are what make it an ideal polymer to form biocompatible complexes suitable for many applications, like controlled drug release formulation.[12] As many other natural polymers, chitosan can acquire positive charges and acts as a chelating agent that selectively binds trace metals,[13] being used as coagulant in wastewater treatment,[14] or in fabrication of composite materials.[15]

Different methods as reverse microemulsion,[16] ionically crosslinked,[17] coacervation or precipitation,[18] and anionic surfactant gelation,[19] have been used to prepare chitosan particulate systems.

In this work, we investigate the interaction between CHI (as biopolymer) and SLES (as anionic surfactant) in aqueous solution. The particles obtained through the interaction at different pressures were then characterized.

RESULTS AND DISCUSSION

The particles form at atmospheric pressure when chitosan solution droplets reach the surface of the surfactant solution. Particles obtaining occurs as a result of the insoluble CHI-SLES complex formation by the diffusion of surfactant in the polymeric solution, followed by a cross-linking mechanism implying electrostatic as well as hydrophobic interactions. Thereby, liquid-liquid phase separation occurred, the chitosan gel was coagulated to form quasi-spherical uniform chitosan gel capsule with a skin layer, which then thicken in time, forming in this way the particle.

The particles formation stages were monitored by video enhanced microscopy by using a Philips videocamera for 1 hour, and then the details regarding the aspect of polymer-surfactant complex were used to plot the CHI-SLES phase diagram. The phase diagram was drawn by using samples whose concentrations increased from one to another by an increment of 0.14 % (w/v) for CHI and by 0.04 % (w/v) for SLES.

The CHI-based capsules obtained by this interaction have different forms. Depending on CHI-SLES complex formation that is induced by the weight ratio between the structural units of chitosan and the surfactant, there are several existence domains in the phase diagram (Fig. 1), namely: a) monophasic (homogenous and clear) system within domain C; b) precipitates (preceded by a significant turbidity) within domain PP; c) formation of gel-type membranes within domains PE (particles with excrescence), SP (spherical particles) and NSP (nonspherical particles).

At low surfactant concentrations (0.2% - 1.4%), in the PE domain, the droplets tend to expel their inside liquid to the outside and form an excrescence (Fig. 2a), while at high surfactant concentrations (3-4%), in the NSP domain (Fig. 2c), the droplets shrink. Within SP domain the formed particles are quasi-spherical and have a maximum stability (Fig. 2b).
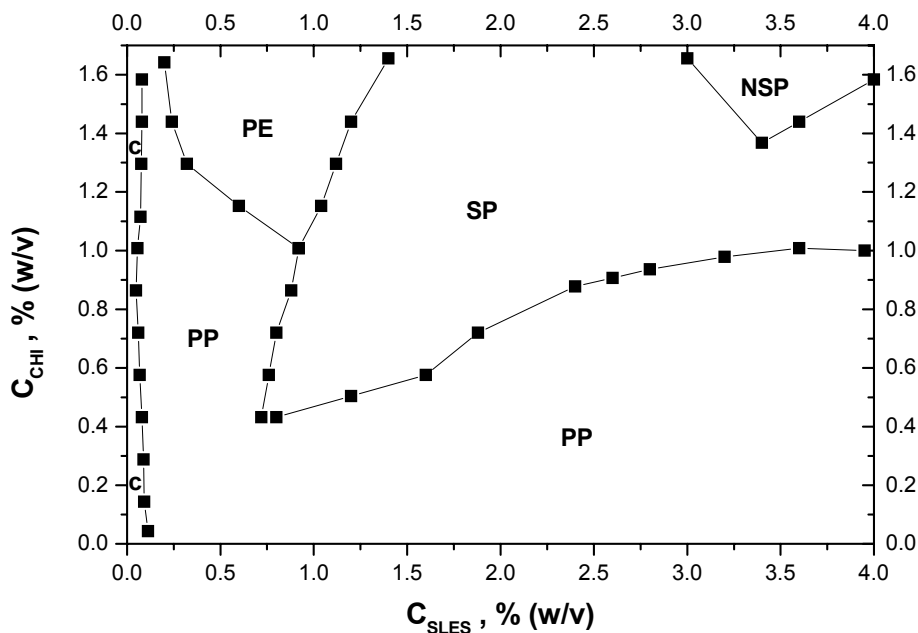
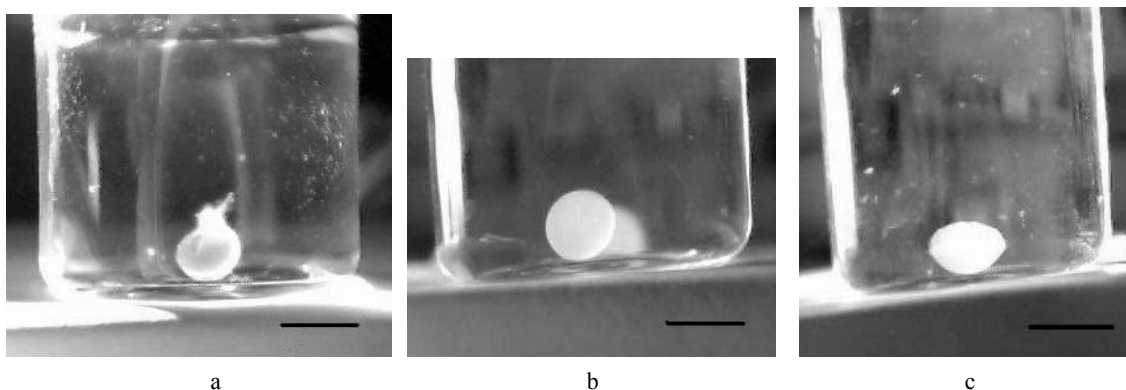Fig. 1 – Phase diagram of aqueous CHI-SLES system.

Fig. 2 – The appearance of CHI-SLES particles: a) particles with excrescence (PE);
b) spherical particles (SP); c) nonspherical particles (NSP). Bar = 5 mm.

The capsules have a low mechanical strength because of the low thickness of the formed films. One possible explanation for particles obtaining is based on the important role of surfactant micelle shape in the physical binding of chitosan to form surfactant insoluble complex. SLES concentrations of 0.72 % (w/v) at which stable spherical particles (SP domain) start to form is noticeably higher than 0.0008M (about 0.032% w/v), its CMC value in water.[20] So, at concentration of 0.72% (w/v), SLES is in micellar form, which favors the cross-linking with chitosan molecules. That is why the surfactant needs to be in the micellar form to obtain particles. Considering the phase diagram shown above, fine particles are obtained at much lower concentrations of chitosan (starting from 0.025%), which are 15 times smaller than the concentration at which the formation of stable particles begins (SP domain).

Depending on pre-expansion pressure applied to spraying the SLES solution, fine particles of different sizes were obtained. Measurements of dynamic light scattering (DLS) and zeta potential revealed a direct connection between the applied pressure of synthesis and the properties of the obtained particles. We observe that the particle size decreases with increasing the spraying pressure of surfactant in polymer solution (Fig. 3). Depending on the spraying pressure (200-500 N/cm^2), small particles of diameter ranging between 425 and 520 nm were obtained.

Thus, for a series of measurements performed on particles obtained at 200 N/cm^2, the particle size ranges between 490 and 540 nm, with an average diameter of 520 nm (Fig. 4).
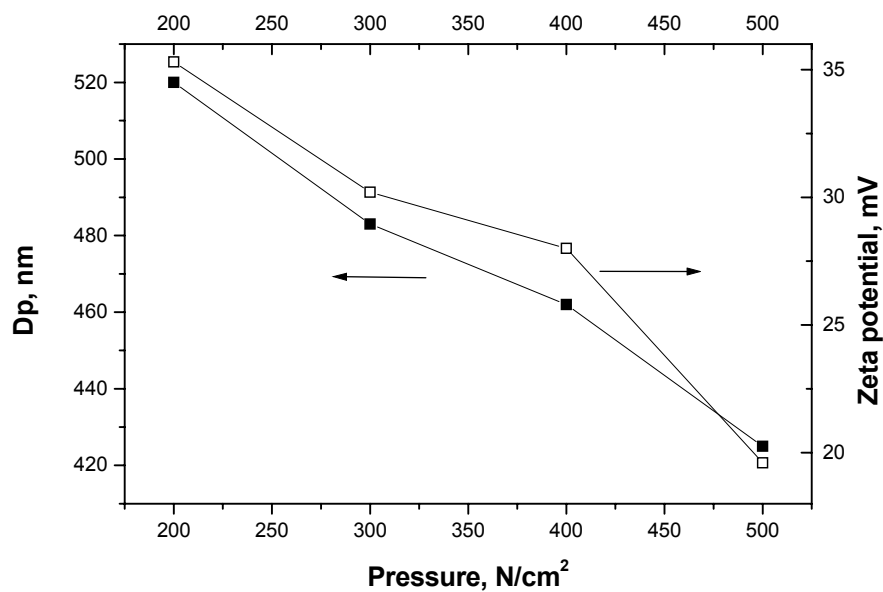
Fig. 3 – Effect of pre-expansion pressure on the average particle diameter (Dp) and zeta potential.
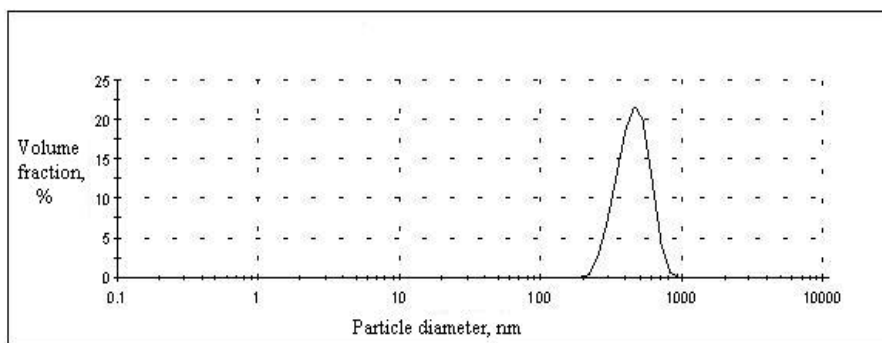

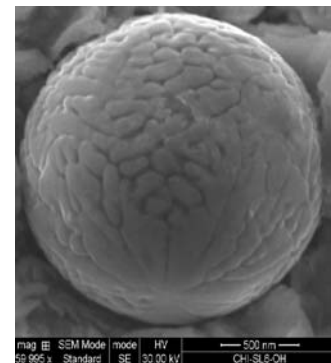Fig. 4 – DLS size distribution for CHI-SLES fine particles prepared at 200 N/cm^2.

Fig. 5 – Microphotograph of CHI- SLES fine particles obtained by spraying.

The CHI-SLES particles are positively charged, and zeta potential decreases with lowering of average diameter of the particles. Zeta potential can influence the stability of the particles in the liquid phase.

The optimum concentrations domain where fine particles were obtained falls in range 0.025% -0.05% (w/v) for CHI, and 0.1-1.0% (w/v) for SLES.

On the other hand, Scanning Electron Microscopy (SEM) shows that the particles have quasi-spherical shape with diameters of 500-1700 nm. These values are somewhat larger than those obtained by DLS measurements.

Fine particles were also derived by dropping and mixing the components at high stirring. Using this method, a SLES solution of 0.4% (w/v) was dropped into a mixture of chitosan (0.05%, w/v)

and acetic acid (0.5%, w/v) at weight ratio 1:1, under vigorous stirring at 10,000 rpm for 30min. The obtained particles were washed 4-5 times with Milli-Q water, centrifuged, separated from the liquid phase, and freeze-dried.

These particles are larger than those obtained by high-pressure method and are characterized by a narrower size distribution (900-1900 nm in diameter), with an average diameter of 1002 nm, as resulted from DLS measurements (Fig. 6).

The SEM investigations confirmed the average dimensions obtained by DLS measurements and revealed a pellet shape of the particles (Fig. 7). The interaction between chitosan and sodium laureth sulfate was studied on lyophilized samples by using FTIR spectroscopy.
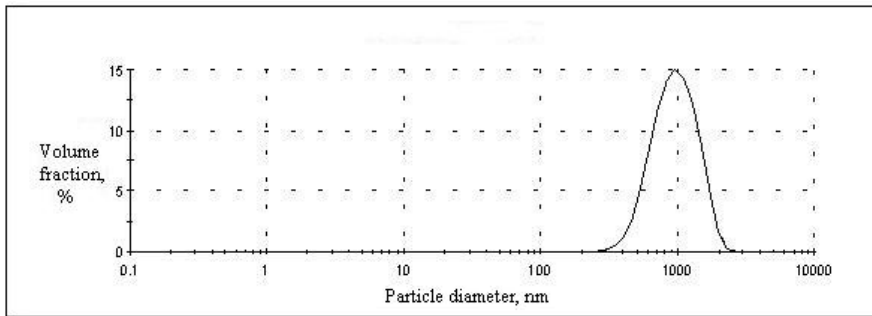
Fig. 6 – Size distribution (DLS) for CHI-SLES fine particles prepared at high stirring.
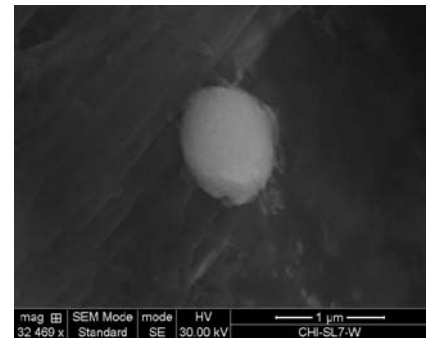

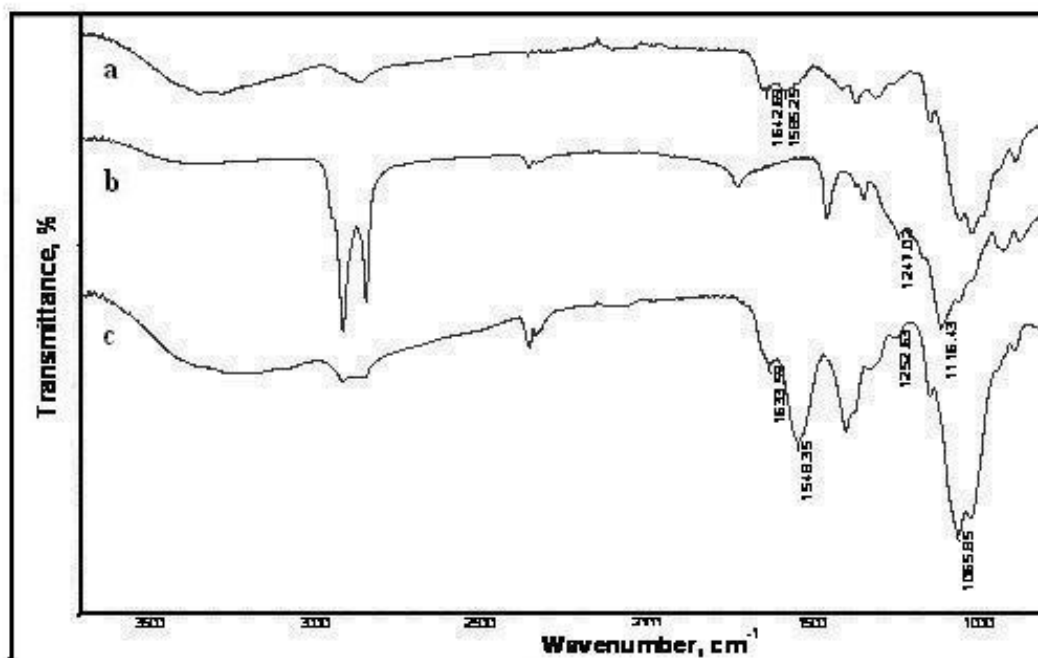Fig. 7 – Microphotograph of CHI- SLES fine particles.

Fig. 8 – FTIR spectra of CHI (a), SLES (b) and CHI-SLES particles (c).

The FTIR spectra suggest that the interactions between CHI and SLES have occurred during the CHI-SLES particle formation. It is most likely that the protonated CHI in the acetic acid solution electrostatically interacts with SLES anions, as shown in the Fig. 8 resulting in the obtaining CHI-SLES complexes as particles. Thus, the characteristic peaks of CHI at 1642 cm^{-1} for the –NH bending vibration and at 1585 cm^{-1} for the –NH deformation vibration of the amino groups were affected and shifted to 1633 and 1548 cm^{-1}, respectively, in the spectrum of the CHI-SELS particles. On the other hand, the characteristic peaks of SLES at 1116 cm^{-1} for -SO_3 vibrations were affected and shifted to 1065 cm^{-1} in the spectrum of CHI-SLES particles, and the 1247 cm^{-1} for S=O vibrations were affected and shifted to 1252 cm^{-1} in the spectrum of CHI-SLES particles. These findings show a possible binding of the anionic surfactant onto positively charged chitosan by electrostatic interactions.

According to the present study, a model of CHI-SLES interaction to result the corresponding CHI-SLES complex is schematically depicted in Fig. 9. Based on that, the hydrophilic head of SLES is attached to CHI and the hydrophobic tail of SLES may participate in micelles formation together with the surfactant molecules occurring in bulk solution.
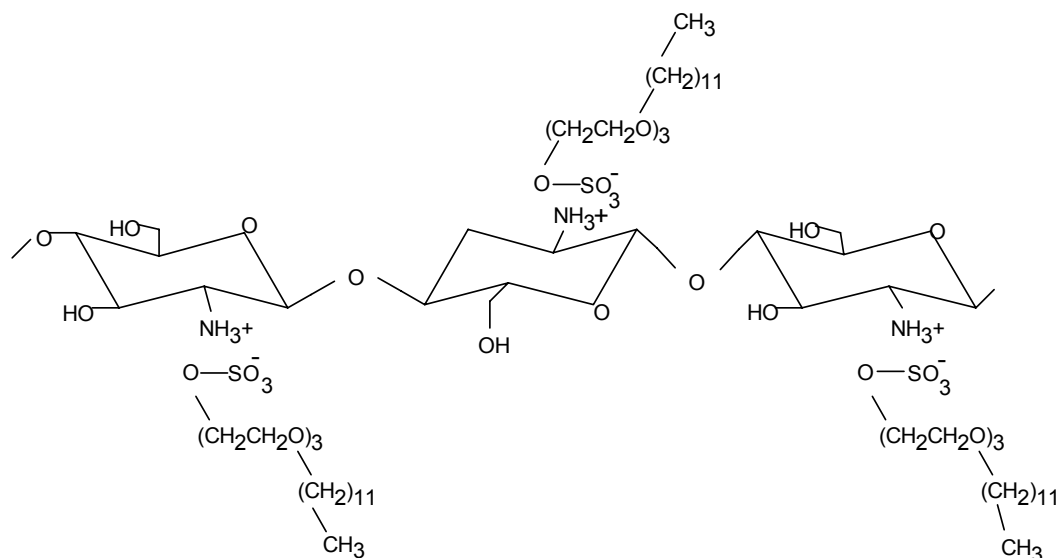
Fig. 9 – Proposed model of CHI - SLES complex structure.

EXPERIMENTAL

1. Materials

Chitosan (CHI) with low molecular weight (M_w = 22±5 kDa) from shrimp shell with a deacetylation degree of 75% was supplied by Aldrich (Germany) and it used without further purification. Sodium laureth sulfate (SLES) 70% was obtaining as sample from Cognis Company Co Ltd. Roumania. Carbon dioxide (CO_2) with 99.9% purity was purchased from Linde Gas Roumania. The pH of the solutions is adjusted to the required value with acetic acid 0.5% (v/v) and NaOH 0.1N solutions. The water used in the experiments was Milli-Q ultrapure filtered.

2. Obtaining of the particles

2.1. At atmospheric pressure. The chitosan stock solution was obtained by dissolving 2g of chitosan in 100 mL of aqueous acetic acid solution 0.5% (v/v), under magnetic stirring at 300 rpm for 24h at room temperature. The CHI-SLES particles are instantaneously formed by spraying 20 mL chitosan solution 0.05% (w/v), preheated 1h at 40°C, through a syringe needle of 30 mm length and 0.4 mm diameter, into 20 mL SLES aqueous solution 0.1% (w/v). The distance from the needle to surface of polymer solution was of about 20 mm. The obtained particles were separated by centrifugation. They are washed 4-5 times with 100 mL Milli-Q ultrapure water on a microporous filter, then with ethanol to remove traces of surfactant. Finally the wet particles were freeze-dried (-55°C for 26 hours) using an ALPHA 1-2 LD plus system.

2.2. At high pressure. In order to obtain fine particles, an experimental apparatus equipped with a high pressure cell was used. The surfactant was sprayed, using high pressure of CO_2, into biopolymer solution bath, through a stainless steel capillary nozzle. Carbon dioxide is used as propelling gas because it is nontoxic, nonflammable, inexpensive, environmentally benign, and does not react with biopolymer chitosan or with anionic surfactant sodium laureth sulfate.[21] The obtained fine particles were collected from the solution through centrifugation at 9000 rpm for 60 min. Supernatants were discarded, and the CHI-SLES fine particles were extensively rinsed 4-5 times with Milli-Q water, and then with ethanol to remove any trace of surfactant, followed by freeze-drying process at -55°C for 26 hours. Dried particles were redispersed in Milli-Q ultrapure water, and then subjected to ultrasonication before DLS measurements being performed.

3. Characterization of the particles

The Fourier Transform Infrared (FTIR) spectra were recorded by using a Nicolet iN10 FT–IR microscope with iZ 10 external module, in the 550-4000 cm^{-1} wavenumber range, at a spectral resolution of 4 cm^{-1}. The size and morphology of particles were determined by scanning electron microscope Quanta 3D FEG 200/400. Measurements for determination of mean diameters and zeta potential of the particles by dynamic light scattering (DLS) were performed using a Zetasizer Nano from MALVREN.

CONCLUSIONS

The result of interaction between positively charged biopolymer (chitosan) and the anionic surfactant (sodium laureth sulfate) is a complex obtaining in the form of particles depending of pressure conditions.

At atmospheric pressure, based on chitosan/ surfactant weight ratio, CHI-SLES complex was resulted as soluble form, precipitate or stable particles.

The CHI-SLES complex at high pressure takes the form of fine particles; the more increase of spraying pressure, the lower particle size is obtained.

The obtained fine particles carry positive electric charge, and are of micrometric size, ranging between 500 and 1900 nm.

The FTIR spectroscopy supports the electrostatic interactions between sodium laureth sulfate and chitosan; based on these reasons, a model of CHI - SLES complex structure was proposed.

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