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From compressibility to structural investigation of sodium dodecyl sulphate — Part 1: Powder and tablet physico-chemical characteristics

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Abstract

As a part of a study on detergent tablets, investigations were carried out to elucidate the compression behavior of a powdered surfactant, sodium dodecyl sulphate (SDS), based on a comparison with the main component of the formulation, i.e. the chlorine provider (DCCNa). The compacted SDS exhibited poor cohesion as well as delayed dissolution whatever the compression pressure. The microscopic observations and the mercury porosimetry measurements both demonstrated that a residual porosity existed in the tablets but the dissolution times were always long. A modification of SDS in contact with water, forming a structure like a gel, probably occurred, inducing the closing of the pores and thereby limiting the water intrusion into the tablets.

Keywords: Surfactant; Sodium dodecyl sulphate; Physical characteristics; Tensile strength; Dissolution

1. Introduction

Surfactants are present in most cleaning or disinfection products [1]. Depending on the nature of the hydrophilic part of these bipolar molecules, surfactants can be distinguished into anionic, cationic, amphoteric and non-ionic classes. Beyond the specific properties, some common functionalities, such as wetting and soil removal, can be attributed to each class. Anionics are historically the earliest and the most common surfactants [1]. They are usually considered to be the leaders in the detergency field. They are especially beneficial for their excellent detergency action and their efficiency to remove particulate soils. In most cases, liquid formulations are used,

however compacted detergent form presents the advantages to be more reliable to use, easier to dose, and safer for the consumer since there is no spillage or dust [2–4]. Thus, in order to satisfy consumer preferences and environmental requirements, detergent industries have developed for the last 10 years new packaging such as tablets, generally obtained by direct compression of dry powders on rotary machines, adapted for high production rates.

In previous works, effervescent detergent tablets were formulated with a chlorine provider (DCCNa), an anionic surfactant, sodium dodecyl sulphate (SDS), an effervescent couple and a disintegrant agent [5,6]. The present study focuses on SDS tableting behavior by comparison with DCCNa, the major component of the reference formula. The two raw materials were compacted with an uniaxial press, well suited for such products exhibiting binding in the die and sticking to the punch faces. The mechanical properties and the dissolution profiles of the respective tablets were studied.

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2. Experimental

2.1. Materials

The two materials were respectively sodium dodecyl sulphate (SDS — TEXAPON® K12 G) manufactured by Cognis (France) and dihydrated sodium dichloroisocyanurate (DCCNa — ACL® 56) manufactured by Oxychem (USA).

2.2. Methods

2.2.1. Initial physico-chemical characteristics of raw materials

Morphology. Particles morphology and texture were observed using scanning electron microscopy (SEM Stereoscan S260) after a 5-min Au/Pd metallization (Cathodic Pulverizer Balzers SCD040).

Particle size distribution. The particles size distribution of the powders was evaluated with a laser diffraction analyser Mastersizer 2000 (Malvern Instruments Ltd, Worcestershire, United Kingdom) by suspending the particles in the air (dispersion pressure=1 bar; vibration rate=40%). The volume equivalent diameters ($D_{0.1}$, $D_{0.5}$, $D_{0.9}$) as well as the span were calculated from three measurements.

Specific surface area. The specific surface area, quantified by the extend of the powder/gas interface, was determined by

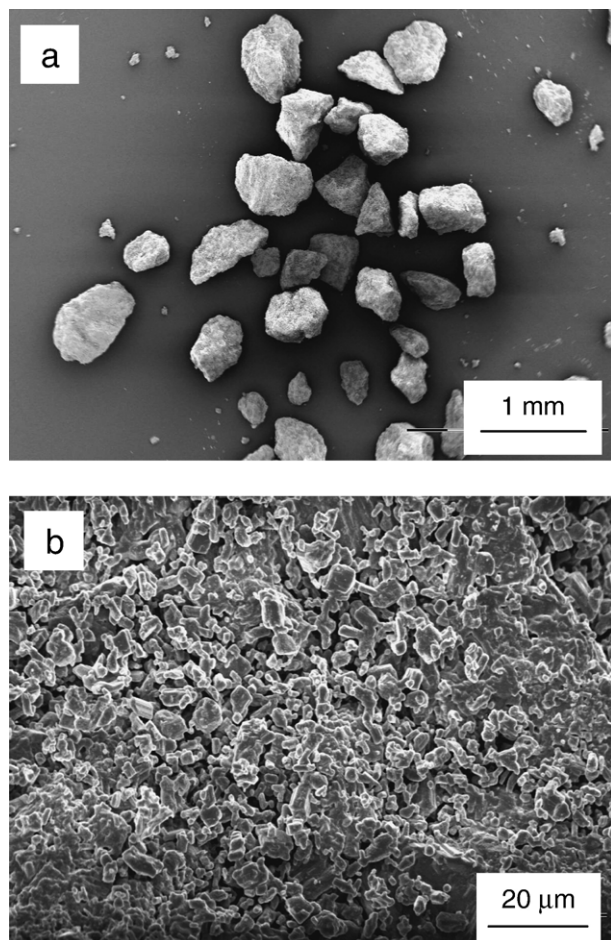


Fig. 1. Morphology (a) and surface details (b) of DCCNa (S.E.M.).

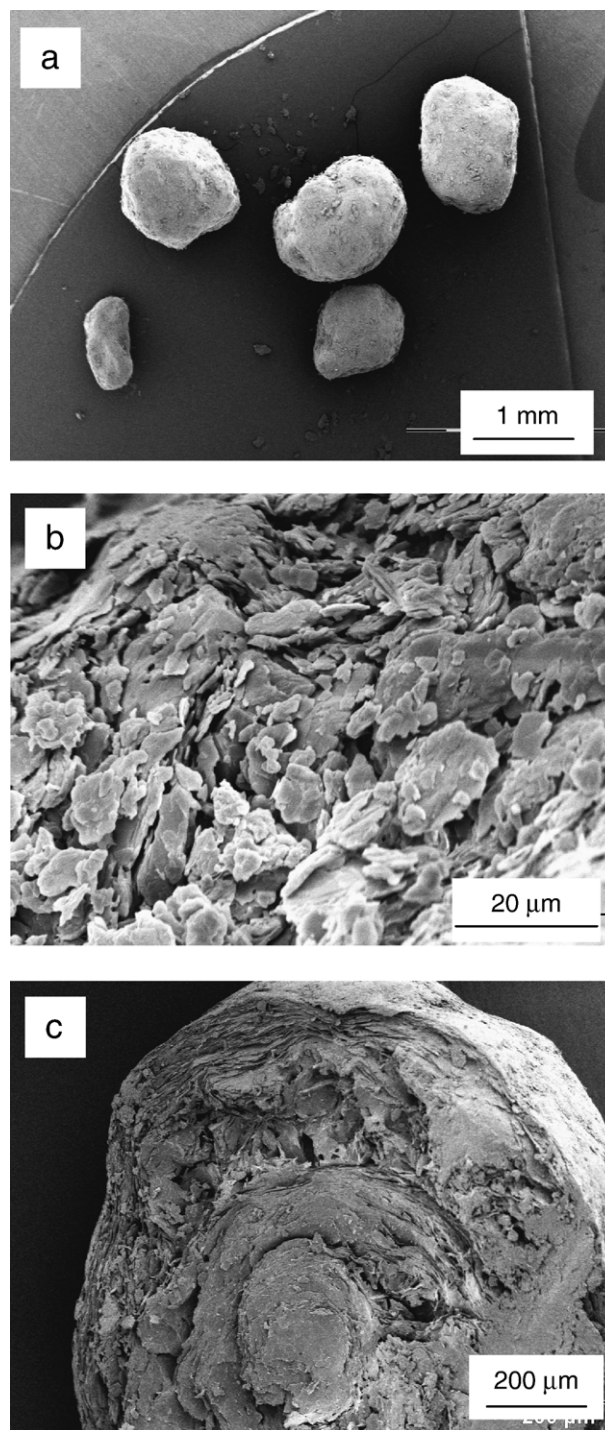


Fig. 2. Morphology (a), surface details (b) and section (c) of SDS (S.E.M.).

nitrogen adsorption on the surface of the material using a Gemini 2360 analyzer (Micromeritics Instruments Inc., Norcross, GA). Prior to measurements, samples were degassed during 10 days at 25 °C under 50 mTorr vacuum (VacPrep 61, Micromeritics Instruments Inc., Norcross, GA). Specific surface area was calculated by the B.E.T multi-point equation [7] in the relative pressure range of 0.05–0.30. The sample weight was adjusted to ensure a surface of at least 1 m² in the cell. The measurements were repeated until stabilization of the value and the mean specific surface area was calculated from the three last stabilized data.

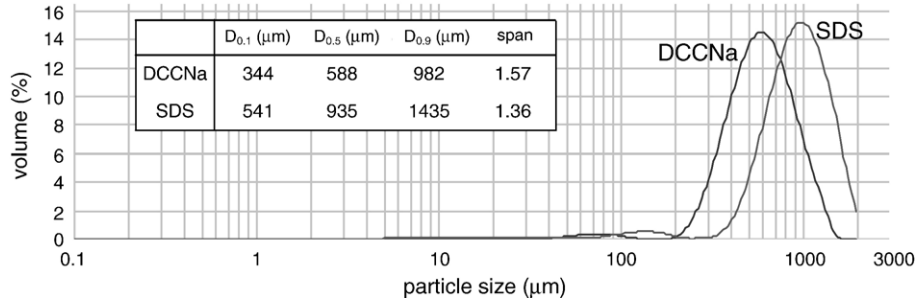


Fig. 3. Particle size distributions of DCCNa and SDS.

Densities. The pycnometric density of the powders (d_{pycno} , g cm^{-3}) was determined using a helium pycnometer (Accupyc 1330, Micromeritics Instrument Inc., Norcross, GA). The samples were degassed under 50 mTorr vacuum (VacPrep 061, Micromeritics Instrument Inc., Norcross, GA) during 10 days at about 25 °C and the measurements were performed using the 10 cm^3 cell [8]. The measurements were repeated until stabilization of the value and the mean pycnometric density was calculated from the three last stabilized data.

The bulk density was determined by pouring 100 g of powder into a 250 ml graduated cylinder (Erweka Model SVM2, ERWEKA GmbH, Heusenstamm, Germany) and measuring the bulk volume V_0 (cm^3) from which bulk density (d_{bulk} , g cm^{-3}) was calculated according to:

$$d_{\text{bulk}} = 100/V_0 \quad (1)$$

Results are the mean of three determinations.

The apparent densities, calculated from the volumes V (cm^3) occupied by the powder bed, were determined from 0 to 1250 taps. Results were expressed as the packing kinetics, corresponding to the curves $\log(V_0/V)$ versus the number of taps. The initial slope and the maximum value of $\log(V_0/V)$ were chosen to express the packing ability of each product and estimate the flow properties of the powders. Three measurements were performed. Moreover, the ability to rearrange was estimated by the difference between the volumes after 10 and 500 taps ($V_{10}-V_{500}$): if this volume was higher than 20 cm^3 , the product presented bad packing properties [9,11].

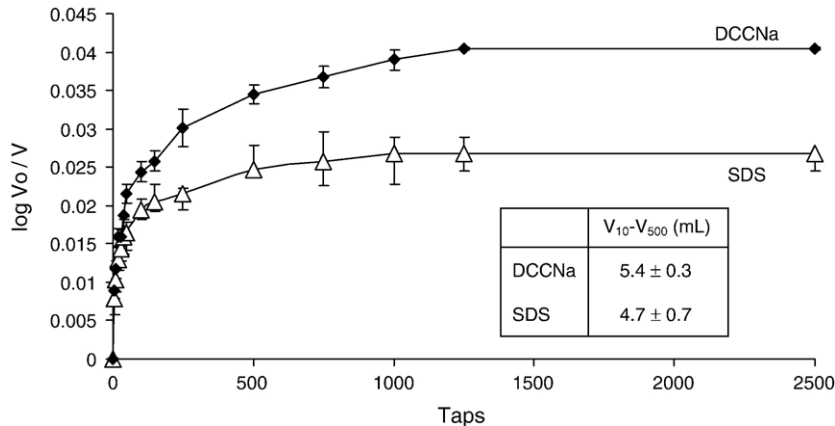


Fig. 4. Packing kinetics of the powders.

2.2.2. Tablet characterization

The global behavior of the materials under pressure was studied using an uniaxial instrumented press, Lloyd 6000R, equipped with a force measuring sensor (0–30 000 N) and an external linear variable differential transformer (LVDT) extensometer (0–20 mm) to accurately measure the forces and displacements during compression and rupture tests. The press is connected to a computer and the results are plotted using R-Control software.

The products were compacted in a 1 cm^3 cell (1 cm of height and 1 cm^2 of surface) with two flat punches. After lubrication of the inner surface with a thin layer of magnesium stearate, the cell was manually filled with an accurate weight of powder determined using the bulk density of the unpacked powders. Pressures from 10 to 295 MPa were studied, with the upper punch speed set at 1.14 mm min^{-1} [12]. These manufacturing conditions were far from the industrial ones but this compaction procedure presented the advantage to allow the compaction of the products without internal lubrication, as the die and punches were cleaned after each tablet.

Mechanical properties. Twenty-four hours after compaction and removal from the cell, diametral compression tests were performed using at least three tablets per pressure. Tensile strength (Rd, MPa) was calculated from the breaking force (Schleuniger-2E, Switzerland) [13,14] according to Eq. (2):

$$\text{Rd} = (2.F)/(\pi.D.h) \quad (2)$$

where F (N) is the maximal diametral breaking force, D (mm) the diameter and h (mm) the height of the tablet.

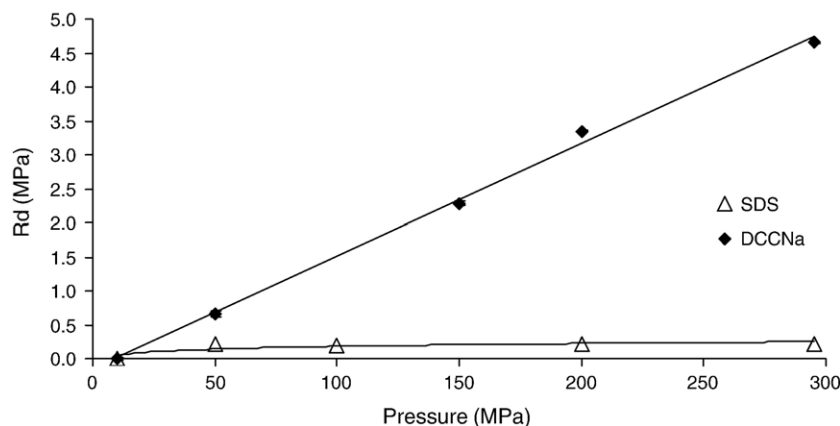


Fig. 5. Tensile strength according to the compaction pressure.

In order to improve mechanical characterization, tablets friability measurements were performed with a friabilator (F1, Sotax, Switzerland). Tests were carried out on a sample of 10 tablets with a drum rotation speed of 25 ± 1 rpm for 100 rotations [15]. At the end of the rotations, tablets were carefully dedusted and the sample was weighed. The friability, expressed as the weight loss percentage, was calculated. The test was repeated three times and the average of the three values was determined.

Dissolution. The dissolution kinetics were determined by conductimetry. Tablets were immersed in 400 ml of distilled water at $21\text{--}23$ °C on a 1.2 mm screen, with magnetic stirring. Conductimetry was evaluated by a conductivity meter (CDM210, Radiometer Analytica, France) with 2-pole conductivity cell with two platinum plates (CDC641T, Radiometer Analytica, France). This cell design allows continuous measurements due to the easy flowing of solution through the two platinum plates. Dissolution time ($T_{\text{dissolution}}$, s) was noted when conductivity was stabilized, i.e. when all the components were dissolved. The measurements were performed in triplicate and only variations higher than 10% were considered as significant. (As a comparison, the same experiment was carried out for the powdered materials).

2.3. Textural investigations

Microscopic observations. Morphology and texture of the tablets were observed using scanning electron microscopy (S.E. M. Stereoscan S260) after a 5-min Au/Pd metallization (Cathodic Pulverizer Balzers SCD040).

Mercury porosity measurements. Porosity measurements were performed using a mercury intrusion porosimeter (AutoPore III, Micromeritics Instruments Inc., Norcross, GA) using pressures from 1 to 10^5 psi. The method consists in measuring the volume of mercury intruded into the pores as a function of the applied pressure. From the total intruded mercury volume (V_{Hg} , cm^3) and the apparent volume of the tablet (V_{tablet} , cm^3), the porosity ($\epsilon_{\text{measured}}$, %) was determined :

$$\epsilon_{\text{measured}} = \frac{V_{\text{Hg}}}{V_{\text{tablet}}} \times 100 \quad (3)$$

$$\text{where } V_{\text{tablet}} = S \times h \quad (4)$$

with S the section of the tablet (1 cm^2) and h the height (cm).

From the Washburn equation [16], the pore size diameters were calculated and the results were expressed as the evolution

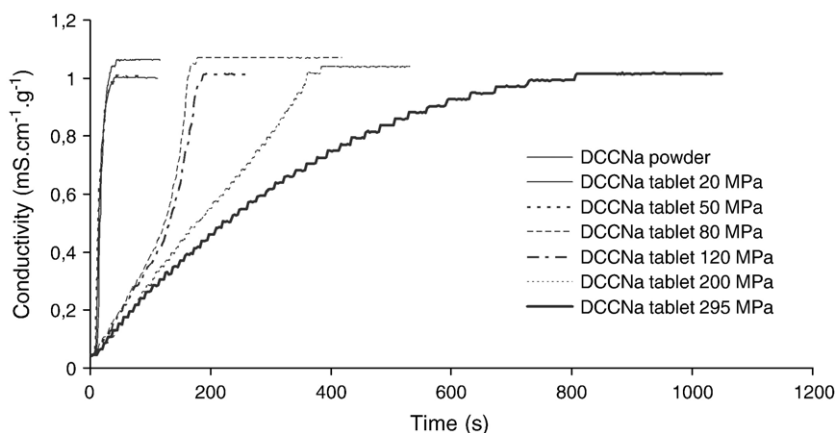


Fig. 6. Dissolution profiles of DCCNa.

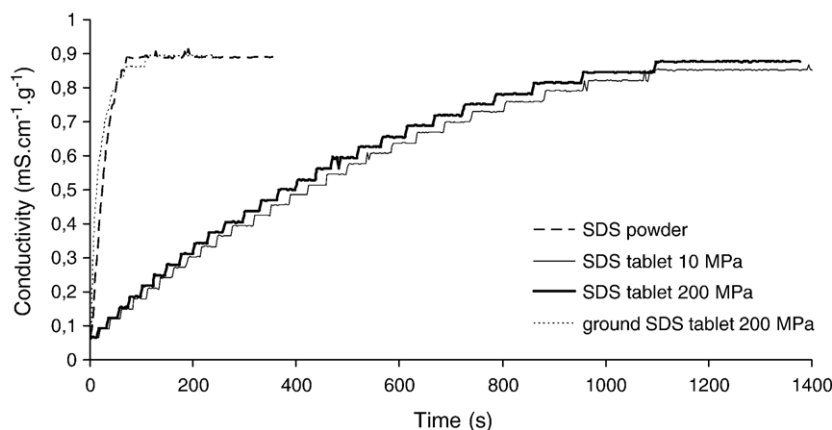


Fig. 7. Dissolution profiles of SDS.

of the differential or cumulated intrusion volumes according to the pore size diameter. Characteristic diameters corresponding to intrusion peaks were deduced from the programs.

3. Results and discussion

3.1. Initial physico-chemical characteristics of raw materials

The particle morphology study exhibited for both raw materials rather large agglomerates from half to 1 mm with isotropic shapes (Figs. 1 and 2). DCCNa surfaces presented asperities and SDS was characterized by an interlocking of plates. The section of SDS agglomerate, highlighted an onion peel-like structure.

The particle sizes were confirmed by laser granulometry determination. The granulometric distributions were monomodal as illustrated in Fig. 3: they allowed the calculation of the median diameters respectively $935 \mu\text{m}$ and $588 \mu\text{m}$ for SDS and DCCNa and of the other granulometric characteristics precised in Fig. 3.

SDS presented a small specific surface area ($0.195 \text{ m}^2 \text{ g}^{-1}$), that can reasonably be attributed to granulometry and surface features, whereas DCCNa particles developed a higher specific surface area ($1.434 \text{ m}^2 \text{ g}^{-1}$) probably linked to surface asperities described previously (S.E.M., Figs. 1 and 2) [17].

Pycnometric density measurements indicated respectively 2.00 and 1.16 g cm^{-3} for DCCNa and SDS. The bulk densities were about 1 g cm^{-3} for DCCNa and about 0.7 g cm^{-3} for SDS. For SDS, the lower bulk density resulted not only from its lower pycnometric density but also probably from interparticulate frictions.

The evolution of the powder bed apparent density accounted for the packing ability (Fig. 4) of the raw materials and was directly correlated to their physical characteristics: SDS and DCCNa had a flowability well suited to properly fill the dies of the tableting machine [17–19].

3.2. Tablet characterization

3.2.1. Mechanical properties

Fig. 5 illustrates the evolution of tensile strength of SDS and DCCNa tablets according to the compaction pressure, from 10

to 295 MPa. SDS developed low tensile strength (0.2 MPa) all along the tested pressure range compared to DCCNa, whose cohesion increased linearly ($r^2=0.9971$) up to 4.5 MPa. Despite their poor diametral resistance, SDS tablets could be handled without causing cracks and defects.

In order to evaluate more precisely this specific behavior of SDS, tablet friability measurements were performed, indicating the percentage of weight loss during the friability test for

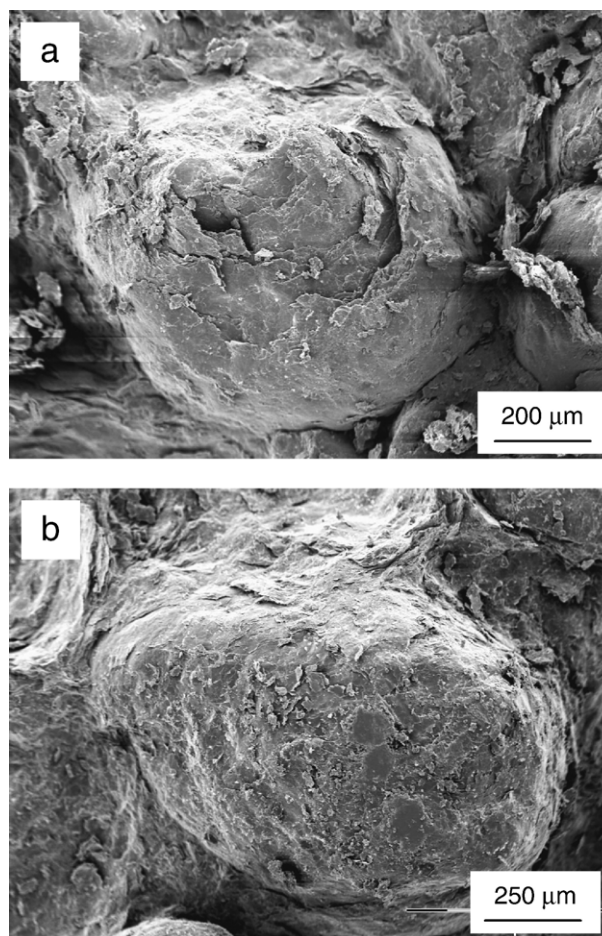


Fig. 8. Microscopic observations of a section of a SDS tablet compressed at 10 MPa (a) and 200 MPa (b).

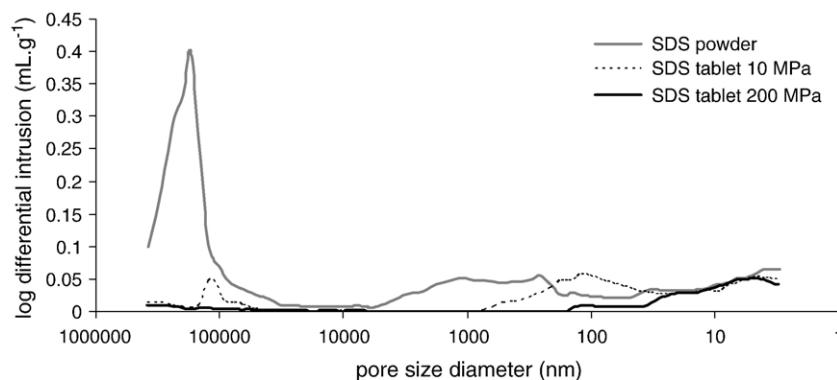


Fig. 9. Mercury porosimetry results of SDS powder and SDS tablets (10 and 200 MPa).

DCCNa and SDS tablets having the same tensile strength (about 0.2 MPa). Results showed that despite this same tensile strength, SDS tablets presented a weight loss smaller than DCCNa tablets, respectively 17 and 54%. This confirmed the previous observations on SDS tablets, i.e. a satisfying handling ability despite a low tensile strength.

3.2.2. Dissolution profiles

Figs. 6 and 7 exhibit the dissolution results of SDS and DCCNa according to the compaction pressure.

In the case of DCCNa (Fig. 6), for the low pressures (up to 50 MPa), the tablets were immediately and totally soaked with water, the dissolution kinetics were fast ($T_{\text{dissolution}} < 100$ s). Then, when the pressure, and consequently the compaction ratio, increased, the dissolution occurred more and more slowly and progressively tended towards an erosion mechanism, reaching a dissolution time of about 800 s. In fact, from 20 to 295 MPa, the porosity of DCCNa tablets decreased from 35 to 7%, limiting such a way the water uptake and so delaying the dissolution [10,20]. On the other hand, for SDS, a same dissolution profile, corresponding to an erosion mechanism, and a dissolution time of about 1100 s, were obtained whatever the pressure (Fig. 7). Only the powdered material exhibited an immediate dissolution ($T_{\text{dissolution}} < 100$ s) due to a large available surface. From the lowest pressure, i.e. 10 MPa, up to the highest, tableting conferred to SDS a same solid texture leading to a similar dissolution behavior. After the grinding of the tablets, the dissolution kinetics was superimposed with the initial dissolution profile of the raw material, suggesting that the dissolution was clearly related to the available surfaces.

Thus, these same profiles from 10 to 200 MPa could suggest that all tablets presented the same porosity and the high dissolution time could indicate that all the pores were closed, responsible for wettability and dissolution. Another hypothesis could be that SDS could swell or present hexagonal phases on contact with water, closing the porosity during the dissolution [21,22].

3.3. Textural investigations

Qualitative microscopic observations of initial SDS particles (Fig. 2) and of a section of a SDS tablet (Fig. 8), compressed at 10 and 200 MPa, showed that the particles were almost

unchanged by compaction whatever the pressure, considering both average size and shape. It revealed also the presence of porosity inside the tablets.

In order to quantify the porosity, the pore size distribution was determined by mercury porosimetry (Fig. 9). From the intruded mercury volumes, respectively 0.099 and 0.033 cm³ g⁻¹ at 10 and 200 MPa, the total porosities ($\epsilon_{\text{measured}}$) were deduced: 10.9 and 5.8%. They confirmed the porosity on S.E.M. The porogram at 10 MPa exhibited three populations of pores around 100 000, 100 and 5 nm whereas at 200 MPa, only the population around 5 nm remained. Thus, we could establish that the pressure increase from 10 and 200 MPa densified the powder bed by filling the 100 000 and 100 nm porous populations [23–25] whereas in the same time, the third population around 5 nm was unchanged. These residual porosity around 5 nm could be an intragranular porosity resulting from fragmentation during the progressive densification but this hypothesis is weakly relevant at 10 MPa. The powdered SDS porogram (Fig. 9) indicated first a high intrusion volume, corresponding to the powder bed porosity for the highest pore size diameters (about 200 000 nm), and then two peaks around 1000 and 5 nm, that might be attributed respectively to intergranular and intragranular porosities. Thus, in the tablets, the small porosity at 5 nm, already existing inside the initial particles, corresponds to intragranular porosity but is not due to fragmentation. These observations are in accordance with the singular texture, in onion like structure of SDS powder, seen in Fig. 2.

4. Conclusion

This study pointed out clear differences between the two materials: for the DCCNa, the tensile strength and the dissolution time progressively increased with the pressure whereas the compacted SDS exhibited poor cohesion as well as delayed dissolution whatever the compression pressure. The microscopic observations revealed the presence of porosity inside the SDS tablets. The quantification by mercury intrusion showed that at 10 MPa, the porosity was higher than at 200 MPa. Nevertheless, these pores did not reduce the dissolution time. Thus, it may be suggested that the SDS was modified in contact with water, forming a structure like a gel, which closed the pores and so limited the water uptake into the tablets. At last, this work evidenced the singular characteristics

of SDS (integrity of the particles and low tensile strength whatever the pressure). This particular behavior has been investigated through an improved compressibility analysis and will be presented in the second part.

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