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## Rheological and microstructural properties of sepiolite gels. Influence of the addition of ionic surfactants

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### ABSTRACT

The present study is focused in the rheological and microstructural characterization of aqueous sepiolite gels and the influence of the addition of ionic surfactants.

Stable sepiolite gels were prepared using a high-shear homogenization process.

The rheological characterization of sepiolite gels reveals shear thinning behaviour. It was observed that yield stress was very influenced by the addition of ionic surfactant.

Cryo-SEM micrographs of sepiolite gels are in good agreement with the rheological behaviour.

It has been shown that is feasible to obtain sepiolite gels with tailored rheological properties as function of the type and amount of surfactant added.

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### Introduction

Sepiolite is a phyllosilicate formed by two tetrahedral layers. Between them there is an octahedral sheet of  $Mg^{2+}$  cations. On a larger scale, sepiolite has a fibrous or acicular structure with hollow channels in the direction of the fibre, which gives it particular rheological properties as well as enabling its use as an adsorbent and catalyst [1].

Thanks to these physical properties sepiolite has many uses and applications such as drilling fluids, agricultural and pharmaceutical products and cosmetics [2–4]. When aqueous suspensions of sepiolite fibres are subjected to high-energy homogenization or sonication sepiolite-gels are obtained due to the reduction in the size of sepiolite particles [5,6]. Sepiolite gels have industrial applications such as pesticide formulations [4]. Furthermore, sepiolite is a promising nanomaterial for use in advanced applications such as polymer-clay nanocomposites, bio-nano-hybrid materials or as a support for nanoparticles [3,7–9].

In all these applications control of the rheological properties are of key importance. Thus, several work has been devoted to the study of the rheological properties of sepiolite suspensions and gels [6,10–13]. Previous works reported that several factors such as pH and surfactant adsorption influenced on the rheological and microstructural properties of sepiolite gels and suspensions. For

instance, Cinar et al. [12] show that the highest viscosity values of sepiolite gels are obtained at the natural pH of sepiolite between 8 and 9. Furthermore, Tunç et al. [13] studied the influence of surfactant adsorption on the rheological properties of sepiolite suspensions. The present study expands our knowledge concerning these systems by analysing the influence of the addition of cationic and anionic surfactant on sepiolite gels rather than sepiolite suspensions.

It is well known that surfactants adsorb onto the sepiolite surface. Thus, several works have been devoted to the study of the adsorption isotherms of anionic, non-ionic and cationic surfactants onto the sepiolite surface in the past two decades [14–16]. On the one hand, it has been shown that anionic surfactants adsorb onto sepiolite at its natural pH even when it is negatively charged. Adsorption occur in three stages: in the first one the anionic head group of the surfactant interacts with  $H^+$  of the bound or zeolitic waters and with  $Mg^{2+}$  cations of the sepiolite; in the second one surfactant chain interaction leads to hemicelle formation and finally an adsorption plateau is achieved at surfactant concentration close to the surfactant critical micelle concentration (CMC) [15]. On the other hand, the cationic surfactant's adsorption isotherm belongs to type H according to the Giles classification, i.e. the solid has great affinity for the solute. Furthermore, adsorption quantities exceed the cation exchange capacity (CEC) of sepiolite [14,16].

Changes in physico-chemical and rheological properties of sepiolite suspensions upon surfactant addition are related to the microstructural modification of clay suspensions. Therefore, the

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direct visualization of the microstructure is of key importance to gain a deeper understanding of the mechanism involved in this process. Nevertheless, sepiolite suspensions micrographs shown in previous studies have been obtained by conventional electron microscopy where water must be removed from the samples prior to obtaining the images. This is an important drawback, since the native state of the suspensions is affected. In order to avoid this experimental limitation cryogenic scanning electron microscopy (cryo-SEM) has been used recently to study the microstructure of clay gels and slurries in their native state [17,18]. As far as we are aware, these are the first cryo-SEM images of sepiolite gels.

In the present work, sepiolite gels obtained by high shear homogenization were studied. Firstly, experiments were carried out to study the stability and  $\zeta$ -potential of sepiolite gels with and without anionic (SDS) and cationic (CTAB) surfactants. Subsequently, complete rheological characterization of these gels was carried out by means of small amplitude oscillatory shear measurements and flow curves. From the latter, the yield stress value was determined and the influence of surfactant concentration and charge was studied. Finally, cryo-SEM images allow us to obtain a direct visualization of the actual sepiolite gels which can be related to the rheological properties in each case.

## Materials and methods

### Materials

A commercial powdered sepiolite, Pangel S9 from Tolsa group (Vallecas, Spain) was used. According to its datasheet this sepiolite has a particle size distribution (by wet sieving) in which more than 90% of the total particles are finer than 5  $\mu\text{m}$  and with a surface area of 320  $\text{m}^2/\text{g}$  according to the BET method using  $\text{N}_2$  as adsorbent. Furthermore, from X-ray diffraction no other phase apart from sepiolite was detected. The chemical composition was obtained by means of X-ray fluorescence and it is shown in Table 1.

Sodium dodecylsulfate (>99%) (SDS), MW = 288.37 g/mol and cetyltrimethylammonium bromide (>99%) (CTAB), MW = 364.45 g/mol were purchased from Sigma Aldrich and used without further purification. Ultrapure water, obtained by using a Milli-Q water purification system was used. All measurements were carried out at 20 °C.

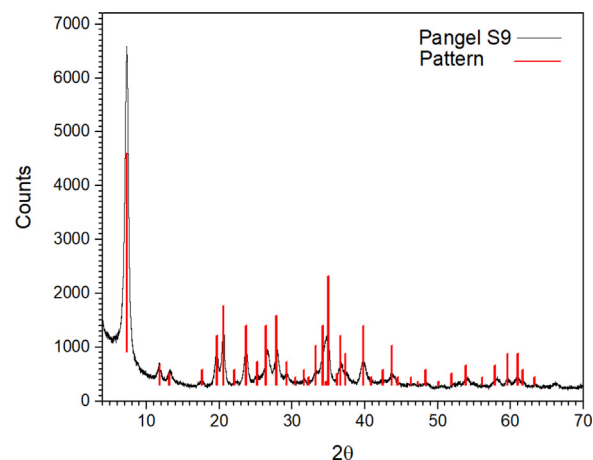
### X-ray diffraction

A powder diffractometer model "D8I-90" from Bruker was used. A standard semi-quantitative methodology was carried out with the following conditions:  $2\theta = 3\text{--}70^\circ$ ; step = 0.015°;  $t = 0.1$  s and X-ray tube operating at 40 kV and mA. The diffraction pattern was compared with an internationally recognized standard for sepiolite. As shown in Fig. 1 a good agreement was found and there was no evidence of the presence of phases apart from sepiolite.

**Table 1**  
Chemical composition of sepiolite Pangel S9.

Compound	Relative concentration (%)	Error (%)
SiO <sub>2</sub>	57.3	0.7
MgO	23.52	0.16
Al <sub>2</sub> O <sub>3</sub>	2.17	0.04
K <sub>2</sub> O	0.65	0.02
Fe <sub>2</sub> O <sub>3</sub>	0.61	0.04
CaO	0.22	0.01
Na <sub>2</sub> O	0.05	0.01
P <sub>2</sub> O <sub>5</sub>	0.03	0.01
LOI <sup>a</sup>	16.46	–

<sup>a</sup> Lost on ignition.



**Fig. 1.** Comparison between the diffractogram of sepiolite sample (black line) and the standard diffractogram of sepiolite (red line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

### X-ray fluorescence

A Analytical AXIOS X-ray fluorescence spectrometer was used. This device is able to quantify major elements (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P) in the form of the following oxides: (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MnO, MgO, CaO, Na<sub>2</sub>O, K<sub>2</sub>O, TiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub> and SO<sub>3</sub>). Table 1 shows the composition in wt.% for the sepiolite used in the present study.

### Sepiolite gel preparation

Sepiolite gels were prepared using a high-shear homogenizer (Ultra-Turrax, T25). The mechanical energy generated allows clumps and clusters of clay particles to break down, strengthening the interaction between the water and the surface of the sepiolite particles and, therefore, increasing the stability and consistency of the gel. Sepiolite concentration was fixed to 3 wt%. which was found to produce gels in previous works [5,11]. The sepiolite solution was sheared for 20 min at 21,000 rpm. Surfactant (SDS or CTAB) was slowly added once the gel was formed and stirred for 15 min with a magnetic stirrer. Final surfactant concentration was adjusted between  $1 \times 10^{-3}$  and  $1 \times 10^{-2}$  mol/L, this surfactant concentration range being chosen in accordance with previous results for bentonite and sepiolite suspensions [13]. Finally, gels were stored for 24 h at 25 °C before measuring in order to mature the gel, thus achieving a maximum level of the viscosity in the samples [5,11].

### Rheological measurements

The rheological measurements were carried out using a controlled stress rheometer (Mars I, Thermo-Haake). All rheological tests were performed at 20 °C, with 10 min of equilibration time, using a solvent trap to inhibit evaporation and were repeated three times.

### Small amplitude oscillatory shear (SAOS)

A serrated plate and plate geometry (60 mm diameter) was used and the small amplitude oscillatory shear measurements were performed using a frequency sweep (3–0.01 Hz) obtained with an oscillatory stress amplitude well within the linear viscoelastic range (LVR) according to stress sweeps conducted at 1 Hz.

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