



# Effect of water soluble molecules on the stability and flexibility of lyotropic lamellar structures. Polymer molecular weight influence

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## ABSTRACT

Two neutral hydrophilic substances, acrylamide and the corresponding homopolymer, polyacrylamide, with different molecular weights, have been incorporated in the lamellar liquid crystal formed by the anionic surfactant sodium bis(2-ethylhexyl) sulfosuccinate (AOT) and water. The study of the elastic properties of the lamellae, through the analysis of the power law exhibited by the Bragg peaks, indicates that the presence of monomer does not modify the interaction between the lamellae until near the macroscopic phase separation, whereas the progressive incorporation of polymer weakens the effective inter-layering interaction. A fraction of acrylamide lower than 5 wt% can be solubilized into the lamellar structures and at higher concentrations a macroscopic phase separation occurs. Regarding the polymers, it has been shown that only the chains with coil sizes smaller than the water layer thickness are dissolved between the lamellae, while larger chains segregate with part of the water developing an isotropic phase. Combining small angle X-ray scattering data and the distribution of macromolecular sizes, obtained by size exclusion chromatography, the fraction of polymer excluded from the lamellae has been estimated.

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## 1. Introduction

The mesophases formed by surfactants in water have biological and technological relevance. In the lamellar mesophase, surfactant molecules stack together to form parallel bilayers separated by water layers. It has been extensively studied for a long time because it is a simple model of the biomembranes, and because it appears in many industrial applications as: detergency, emulsification and foaming [1]. They have also attracted considerable attention because of their excellent potential as drug vehicles, since molecules such as chemical drugs, peptides and proteins can be solubilized, being protected from hydrolysis or oxidation [2]. Recent studies propose the lamellar phase as a good system for cutaneous drug delivery [3–5].

In these applications they act in the presence of other molecules, and it is well known that the presence of a third component leads to dramatic changes in the lyotropic structures, i.e. in the phase diagram. In particular, the use together of surfactants and polymers is rather usual in medicine, food, paints, etc. Therefore, it seems crucial understanding how the polymers interact with mesophases and, consequently, the influence of hydrogen bonding, electrostatic, hydrophobic and steric interactions has been profusely studied [6,7]. In polymer doped lamellar phases, depending on the polymer-bilayer interactions, the polymer can be located in different environments: (i) within the bilayer [8], (ii) distributed

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between the amphiphile layer and the water domains [9], (iii) in the water layers, either adsorbed onto the bilayer [10] or solubilized in the water domains [11], and (iv) finally, a part of the polymer can be solubilized in the water domains, being the rest excluded with a part of the water, giving rise to a polymer rich isotropic phase [12].

Oppositely charged polymers give rise to the formation of nanostructured complexes with lamellar [13], cubic [14] or hexagonal [15] organizations as a result of the electrostatic interactions between the oppositely charged units, and the hydrophobic interactions between polymer backbones and the alkyl chains of the surfactant. These organizations can be tuned by different parameters as: global composition [16,17], length of the surfactant alkyl chain [18], length of the polymer chain [19], presence of co-surfactants [20], macromolecular charge density [21,22] and the ionic strength [23].

Special interest has been devoted to the interaction between neutral polymers and ionic surfactants. In these systems, factors such as the shielding of surfactant charges in the presence of brine [24,25] are important, but the primary driving force is the hydrophobic attraction. As an example, the effect of adding polyethylene glycol (PEG) to the lamellar phase of anionic surfactant Sodium dodecylsulphate has been studied [25–28]. The results revealed that the addition of polymer induces the transformation of  $L_2$  into a vesicular phase. The polymer is solubilized in the water domains of the phase and adsorbed onto the surfactant bilayers, thus stabilizing aggregates of high curvature. The presence of polymer can influence the inter-bilayer interactions and the elastic constants of the bilayers [27]. Ligoure et al. found a decrease of the elasticity of the bilayer when a non-adsorbing water-soluble polymer, polyvinylpyrrolidone, was incorporated in the lamellar phase of the cationic surfactant cetylpyridinium chloride [29].

Ficheux et al. [10] compared the effect of two water-soluble neutral polymers on the stability of the AOT/water lamellar phase: an interacting polymer, PEG, and a noninteracting polymer, polyacrylamide (PA). No perturbation is observed in the presence of PA while PEG strongly affects the interactions occurring in the lamellar phase. They propose that polymer-doped lamellar phases can be obtained in a range of surfactant and polymer concentrations, which depends on the adsorbing or non-adsorbing tendency of the polymer toward the surfactant. In fact they argue that polyacrylamide of molecular weight  $5 \times 10^6$  can be incorporated in the AOT lamellar phase. Afterwards, it has been shown that the confinement of water-soluble noninteracting polymers in the lamellar mesophase depends on the relative size of the thickness of the water layer and the hydrodynamic volume of the macromolecule [30,12]. Therefore, in order to get a deeper insight, in this work we reassess this system, incorporating the acrylamide monomer (A) and its homopolymer (PA) in the aqueous layer of the AOT/water lamellar phase. The aim is to analyze how the concentration of these substances and the polymer dimensions affect the stability of the mesophase and the flexibility of the bilayers. The structure of the mesophase will be determined by small angle X-ray scattering (SAXS) with synchrotron radiation. Furthermore, a geometric model to estimate the amount of polymer incorporated to the lamellae have been developed.

## 2. Experimental

### 2.1. Chemicals

1,4-bis(2-ethylhexyl)sodium sulfosuccinate (AOT), and acrylamide (A), both with 99% purity, were purchased from Sigma. Polyacrylamides (PA) of molecular weight  $M_w = 1500$  (PA1) and  $M_w = 10,000$  (PA2) were provided from Aldrich as a 50% aqueous solution, while PA with  $M_w = 5,000,000$  (PA3) is from Fluka. The polymers PA1 and PA2 were purified by precipitation in ethanol at 0 °C three times, PA3 was used as received. The purified polymers and AOT were dissolved in water and freeze-dried before used. Deionized water (Milli-Q) was employed for the samples preparation.

### 2.2. Polymer characterization

The intrinsic viscosity of polymers was determined in water at 30 °C using the Huggins and Kraemer extrapolations. The viscous average molecular weight was determined by using the Kuhn–Mark–Houwink–Sakurada equation with the exponent  $a = 0.66$  and the constant  $K = 6.8 \times 10^{-4}$  dL/g for PA1 [31], while for PA2 and PA3  $a = 0.8$  and  $K = 6.31 \times 10^{-5}$  dL/g [32].

The molecular weight distributions were determined by size exclusion chromatography (SEC), using an equipment which consists of HP 1100 pump, a Rheodyne injector, a Waters 2414 refractive index detector, and three Ultrahydrogel columns (250, 1000, 2000). The measurements were performed at 30 °C in aqueous 1M NaNO<sub>3</sub> solution as eluent and a flow rate of 0.5 mL/min. A universal calibration with 11 POE narrow standards from Polymer Laboratories (molecular weights ranging from  $1.8 \times 10^4$  to  $1.7 \times 10^6$ ) was employed. The Mark–Houwink equation for the standards in aqueous 1M NaNO<sub>3</sub> solution at 30 °C was experimentally determined, obtaining  $a = 0.74$  and  $K = 1.66 \times 10^{-4}$  dL/g. For PA samples in this solvent and

**Table 1**

Intrinsic viscosity,  $[\eta]$ , viscous average molecular weight,  $\bar{M}_v$ , determined by viscosity. Weight average molecular weight,  $\bar{M}_w$  and polydispersity index,  $r$ , determined by size exclusion chromatography (SEC).

Polymer	$[\eta]$ (dL/g)	$\bar{M}_v$ (g/mol)	$\bar{M}_w$ (g/mol)	$r$
PA1	0.04	500	563	3.6
PA2	0.09	$8.7 \times 10^3$	$4.5 \times 10^3$	7.0
PA3	6.06	$1.69 \times 10^6$	$5.7 \times 10^6$	1.2

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