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MICROSTRUCTURAL STUDY AND MODELLING OF SHEAR-INDUCED PHASE IN SURFACTANT SOLUTIONS

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INTRODUCTION

The shear-induced transition of an originally undisturbed lamellar phase to a vesicle phase has been studied by rheo-optic (Rheo-SANS measurements *in situ*). The study was carried out on a lyotropic lamellar phase, which had been prepared without introducing energy into the system by shearing or stirring. The ionically charged L_α-phase with stacked bilayers is produced by the protonation reaction of a L_3-phase mixed with an ester[1]. If this low-viscous L_α-phase is subjected to shear it is transformed into a highly viscous multilamellar vesicle phase ("onion" phase). The "onions" are polydisperse in size and densely packed which results in elastic properties and a yield stress. We observed that the transformation of the lamellae to vesicles can be characterized by three time constants, which decrease linearly with the shear rate. Moreover, it is shown that the size of the final aggregates (estimated from scattering experiments) is influenced by the shear rate, the charge density, chain length surfactant and cosurfactant, and the ratio surfactant/cosurfactant. Furthermore we fitted the experimental data with an empirical model (Bautista *et al*. 2000)[2] which predicted very well the transition between all the phases.

***Key words*:** Lamellar phase, onion phase, complex fluids and shear thickening.

EXPERIMENTAL METHODS

The tetradecyldimethylamine oxide (TDMAO) was a gift of the Clariant AG Gendorf. It was recrystallized twice from acetone and characterized by the melting point and cmc. 1-hexanol of Fluka and oxalic acid diethylester-solution of Merck were both of p.a. quality and were used without further purification.

The viscosity of the samples were measured by a Bohlin CS 10 stress controlled rheometer by using a couette cell. Neutron scattering cells or couette cells were filled with a L_α-phase (or L_3-phase mixed with the appropriate amount of diethyl oxalate). SANS experiments were performed at the ILL reactor on the line D11 at Grenoble France.

RESULTS AND DISCUSSIONS

In the lamellar phase of the TDMAO/Hexanol and water system, transition from lamellae to vesicle, under flow was observed. In the rheological measurements we found continuous changes for the viscosity with time (figure 1). The lamellar phase at rest shows a low viscosity because some of the bilayers form small multidomains. With shear the bilayers are aligned and rearrangement in largest domains which increase the

viscosity. During this transition the viscosity increases abruptly due to the appearing of a new phase ("onion" phase). Figure 1 also includes contour pattern obtained under shear, which reveal additional information about the structure of the steady state behavior in the different regions. The flow direction in the contour plots is vertical. The first pattern corresponds to the "virgin" lamellar phase formed at the end of the hydrolysis reaction and prior to the shear (t = 0 s). This pattern is completely isotropic since due to the multidomains present in the lamellae. The second scattering pattern was measured around 70 seconds after application of a shear gradient of 1 s^{-1}. It is characterized by two intense peaks perpendicular to the flow direction. This indicates the presence of an ordered texture in the flow direction. During the next minutes of constant shear the high anisotropy decrease and we can associate this with the onset of the transition from lamellae to vesicle, i.e. after this point the perpendicularly oriented lamellae start to break and form vesicles. At longer times the degree of orientation diminishes clearly (fourth pattern) and it is characterized by a scattering ring with only a fairly small degree of anisotropy due to the shear deformation of the vesicles. The scattering patterns presented here confirm the presence of multilamellar vesicles with a similar interlamellar spacing as the previously present lamellar phase.

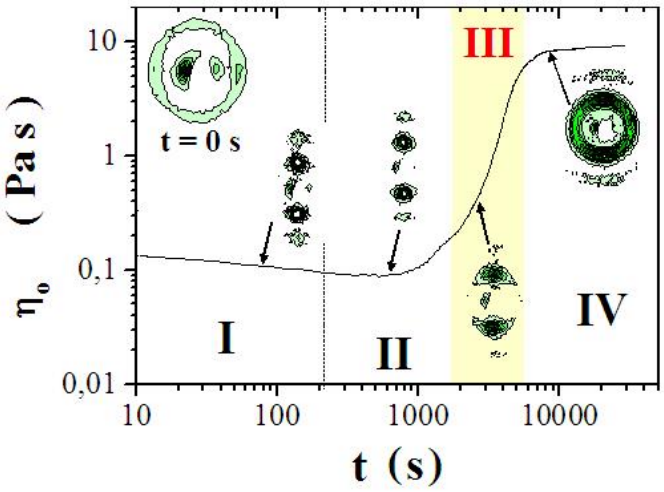

Figure 1. Rheological response of the lamellar phase subjected to a shear rate of 1 s^{-1} at 25 °C.

However we obtained a master diagram where the abruptly increase of the viscosity appear always at the same value of deformation ($\tau \times \dot{\gamma} \sim 2000$). It is independent of the shear rate, charge density and chain length of surfactant (or cosurfactant). We can concluded from the results that the whole process of transition is government for fourth regions, where firstly the original lamellar phase is exposed to shear flow and tend to aligned parallel to the walls, after this moment the lamellae changes their alignment from parallel to perpendicular and begin of the transition from lamellae to vesicle. Finally, the lamellae tend to break up and form vesicles, which by influence of the shear flow tend to from a highly packing structural.

REFERENCES

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