**Budapest University of Technology and Economics**
**Department of Physical Chemistry**

# LAMELLAR LIQUID CRYSTALLINE

# SYSTEMS

Ph.D. thesis

Writen by:

**Tamás Horányi**

Consultant:

**Dr. János Pálinkás**
university docent

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# INTRODUCTION

Nowadays the different lyotrop liquid crystalline systems show an ever increasing importance in cosmetics and household chemical industry. They can be successfully applied for controlled and transdermal drug delivery. Between the dead cells of the stratum corneum there is a liquid crystalline material that protects the lower layer of the skin against the impact of both polar and apolar materials. The only component that relatively freely but in a controlled way can move through this barrier is water. This liquid crystalline layer has a very complex composition and structure, and therefore is not easy to investigate. At the same time the state of this barrier is a very important factor in the health and beauty of the skin.

The ethoxylated fatty acids studied by me can serve as a simple chemical model of this biological system. Concentrated aqueous solutions of these have a lamellar liquid crystalline structure at around 70 w/w % surfactant concentration. (This concentration falls very close to the lipid concentration of the stratum corneum.)

During my work I have studied these systems by different optical and rheological methods. My goal was to understand the above mentioned protecting mechanism of the human skin, and to suggest methods by which this effect can be influenced or reinforced. I have applied static and dynamic rheological measurements, polarised microscopy and small-angle X-ray scattering.

As the function of a biological system is highly determined by its structure, the main goal of the rheological measurements was to clarify the structure dependent mechanical properties of the protecting barrier. By the frequency dependent measurements the so-called rheological fingerprint of the system can be determined. The different mesophases can be distinguished according to this suite of physical properties. At the same time the mechanical model of the studied system can be determined by static measurements.

The optical methods served as a reinforcement of the hypothesis suggested for the microstructure according to the rheological findings. If a system consists of lamellae it must be optically active and therefore can be studied by polarised microscopy. At the same time the regularity and the characteristic lengths (domain sizes and repeat distance) of structure can be determined by small-angle X-ray scattering.

During my work I have suggested a new rheological model that is suitable for the description of the dynamic rheological properties of the above mentioned liquid crystalline systems containing surfactants and some additives. The most important new element of this model was the so-called orientation modulus that is the energy requirement of the domain orientation process under shear.

I have shown that very similar structural changes and domain orientation processes take place in the studied samples during rheological and optical measurements. In case of the optical investigations the initiator of these changes is an interface effect, while during the rheological measurements the process is governed by the shear flow. Comparing the dependence of the time required for the complete pseudo isotropy and the dependence of the orientation modulus on the concentration and polarity we can see a very strong correlation. This means that although these two observations seem first completely different, but their physical background is the same.

**THESIS**

## I. Composition of the model system

1.) **Based on its structural properties I have used many types of ethoxylated aliphatic fatty acids (Synperonic A7, a Synperonic A9, a Synperonic 91/4 and Synperonic 91/5) with different molecular structure to model the lyotrop protecting layer of the human skin.** Number of carbon atoms of the alkyl chains varied between 9 and 15, while the degree of ethoxylation was between 4 and 7. The validity of this choice is reinforced by the fact that the mentioned materials form a stable lamellar liquid crystalline structure around 70 w/w% surfactant concentration that is very close to the concentration of lipids in the mentioned protecting layer.

## II. Investigations by polarized microscopy

Investigation of the process that causes the so-called pseudo-isotropy makes it possible to clarify the mechanism of the domain-orientation caused by surface interactions. It is important to emphasise that in the human skin the layers of the barrier are immobilised too as they are chemically connected to the proteins of the dead keratinocites.

2.) **I have found that the formerly mentioned pseudo-isotropy is suitable for the characterisation of the elasticity and structural stability of the studied systems.** As a numerical measure I have used the time required for the complete darkening of the microscopic picture. In order to investigate the kinetics of the process I have introduced the so-called average brightness which is a general measure of the complex textures found on the pictures. I have found that the decrease of this value can be described by two slow exponential decays following each other. The end of this process is the so-called pseudo isotropy. This finding reveals for a rather complex kinetics which is highly influenced by the properties of the interface. I have produced and applied glass containers with different surface polarity – by introducing silyl groups on the glass interface – and have found that the increase of the number of polar groups on the interface causes the decrease of the time required to reach the pseudo-isotropy. This effect was stronger when the HLB value of the sample was lower. There was a similar regularity when the surfactant in the sample was varied at a given surface polarity. It was always the surfactant with lower HLB value that showed shorter characteristic time.

3.) **When the liquid crystalline samples were added by triblock-copolymers (these were Pluronic L62 and F68; both have PEO-PPO-PEO structures but their HLB-value is different) I have found that their effects was proportional to their concentrations and the observed changes are accordance with the expectations due to their HLB values.**

4.) **Varying the thickness of the sample layer I have found that the ordering effect of the surface can effect only within a limited distance.** Measurements of the same samples by small angle X-ray scattering have shown that this ordering effect diminishes beyond 30.000 double layers. Invariability of the first exponential part of the brightness-time curves can be explained in a way that in the first step the interaction (adsorption) energy is independent on the sample thickness.

5.) **I have found that at higher temperatures the velocity of the darkening increases and the whole process can be described by a first order kinetics.**

## III. Measurements by small-angle X-ray scattering

I have used small-angle X-ray scattering in order to determine the size of the liquid-crystalline domains. Results of these measurements were compared to those of the rheological measurements.

6.) **I have found that the repeat distance of the samples increases with both the length of the hydrocarbon chain and the number of ethoxy groups.** The rather apolar L62 additive decreased while the more polar F68 polymer increased the observed characteristic length. These results indicate that the polar additive fixates and "shrinks" the double layers.

7.) **I have found that the characteristic lengths in the formerly suggested barrier models and in the Synperonic A7 systems studied by me show similar dependence on the water content.** I have rescaled the curves determined from the scattering images back to point focus and used the Scherrer equation to determine the lateral domain sizes. The resulting 140-230 nm size region show a very good agreement with the size of the Oddland bodies.

## IV. Rheological investigations

*Theoretical modelling of the rheological properties*

I have used a special theoretical structural model to describe the frequency-dependent rheological properties of the samples. By means of this mathematical apparatus I was able to reproduce both the loss and storage moduli over the whole frequency range of measurements. There are two time constants in the model that can be interpreted as the relaxation time of the initial elastic deformation and the relaxation time of the bulk phase.

8.) **The domain orientation processes observed in the studied samples were interpreted by the so-called orientation modulus ($G^E$) which is a material constant.** As this quantity corresponds to the energy demand of the domain orientation it can be used as the rheological measure of the structural stability.

*Frequency-dependent rheological investigations*

I have interpreted the effect of the temperature, concentration and the polymer additives by the model parameters fitted onto the results of the oscillatory measurements.

9.) **Determining the orientation modulus of Synperonic A7 solutions with different concentrations I have found, that the highest stability belongs to the sample that contains 70 w/w% surfactant.** The structural stability of the system decreases if the composition differs from this value (within the boundary of the lamellar region in the phase diagram) regardless whether the concentration of the surfactant is higher or lower. **I have found that both the structural stability and elasticity of the samples decreases if the temperature is raised.** The initial elasticity and the orientation modulus show a significant dependence on the chemical structure (HLB value) of the surfactant. The highest elasticity and the most stable structure were observed at the sample with the lowest HLB value.

10.) I have studied the effect of additives by two PEO-PPO-PEO type triblock copolymers with different structures. **I have shown that the more hydrophobic Pluronic L62 additive increases both the stability and elasticity, while the more hydrophilic Pluronic F68 causes the opposite.** The strength of this effect is proportional to the concentration of the additive.

*Time-dependent rheological investigations*

Based on the results of model fitting and some structural properties I have chosen the Burgers model for the description of the results of the creep tests. My goal was to determine the same parameters characteristic for the samples by this model as before by the frequency-dependent measurements. As a basis of the interpretation I have used the initial elasticity, the relaxation time constants of the model, the specific viscosity of the Newtonian region and the residual deformation.

11.) The time constants of the Burgers model show a difference of several orders of magnitude. **According to some structural considerations I have assigned the higher one to the domain orientation process, while the lower one belongs to the initial elastic deformation.**

12.) **I have found that the elasticity of the surfactant systems and their resistance to the shear impacts decreases with the increase of the temperature.** This effect is more pronounced in the case of the surfactants with higher HLB values. **I have found that in the Synperonic A7 systems the concentration dependence of the structural stability and elasticity can be described by a maximum curve.**

13.) By means of the domain size evolution curves determined from the recovery curves **I have determined the sizes of the non disturbed and the decomposed domains. I have found that at room temperature the former falls in the 250-500 nm size region and it is in a good agreement with the one calculated from the results of the small-angle X-ray scattering.** Under shear the domain size decreases, and falls into the 75-125 nm size region

**V. Connection between the results of the rheological and optical measurements**

14.) **I have shown that very similar structural changes and domain orientation processes take place in the studied samples during rheological and optical measurements.** In case of the optical investigations the initiator of these changes is an interface effect, while during the rheological measurements the process is governed by the shear flow. Comparing the dependence of the time required for the complete pseudo isotropy and the dependence of the orientation modulus on the concentration and on the polarity we can see similarity in the curves. This means that although these two phenomena are completely different, but they have a common physical background.

## PUBLICATIONS

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