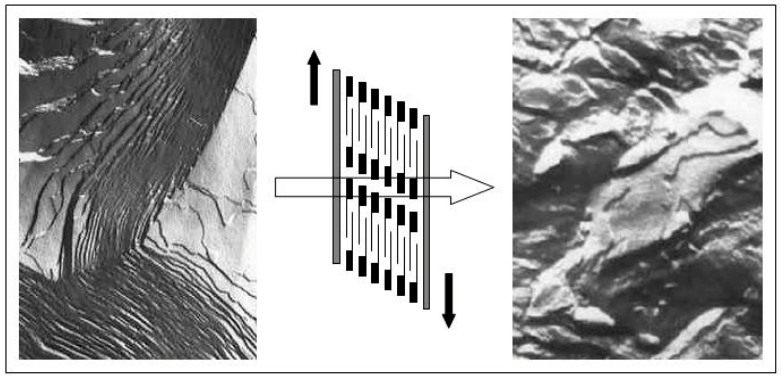
BUDAPEST UNIVERSITY OF TECHNOLOGY AND ECONOMICS
Department of Physical Chemistry

IN SITU INVESTIGATION OF LYOTROPIC SYSTEMS

Ph.D. thesis



Written by:

György Fetter

Consultant:

Dr. Attila Bóta
associate professor

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INTRODUCTION

Molecules having hydrophilic and hydrophobic parts simultaneously are called amphipathic ones. If their hydrophobic chain is large enough, they can form nanometer- and micrometer-scale structures in concentrated solutions. Micelles, lamellar or hexagonal structures are formed, depending on the concentration. These systems are called lyotropic liquid crystals.

In my thesis I have been investigating the lamellar structure of the non-ionic surfactant Synperonic A7-water system and its changes under shear stress and thermal treatment. The Synperonic A7 ethoxylated fatty alcohol is the main component of several household chemicals and cosmetics, thus it was investigated by structure examination and rheological methods. Pálinkás et al. at BUTE Department of Physical Chemistry were studying its rheological features mainly.

I intended to investigate the structural features of this system, utilizing the facilities of the Structure Researching Laboratory of the Department. I wanted to find the origin of the tixotropy of this system, which was verified by several researchers, and the relationship between the shear stress and the inner structure. I supposed, that shear stress causes changes in the nanoscale structure, which can be followed by small angle X-ray scattering (SAXS), thus I considered to use this method.

For these measurements I had to design and build a shear cell, because it was not available from the commercially. This new

equipment is called ”rheoblock” and it is a small and very simple oscillatory viscosimeter. The rheoblock can be placed into the beam of the SAXS apparatus to obtain structural information.

After some SAXS measurements it was discovered, that no significant changes are observable during a short-term shear, while the rheological features were altered significantly. Thus the nanoscale structural investigations had to be expanded to the region of the micrometers. A new version of the rheoblock was constructed for freeze-fracture visualisation of the micrometer-scale domain structures.

The rheoblock was also used to study the 8CB ferronematic liquid crystal. The distribution of the magnetite particles and the effect of shear stress on the lamellar structure were studied.

MATERIALS AND METHODS

Synperonic A7 The general formula of the molecule is:

$$HO\text{-}(CH_2\text{-}CH_2\text{-}O)_7\text{-}(CH_2)_{15\text{-}17}\text{-}CH_3$$

The average ethoxilation grade is 7; the ratio of the C_{13}:C_{15} chains is 66:34.

Small angle X-ray scattering Scattering or diffraction methods give information about the inner structure of the substances. Wide angles correspond to the atomic distances, while the nanoscale colloid measures correspond to small angles. The lamellar structure of the Synperonic A7-water system gives a peak in the SAXS pattern, which can be interpreted by the Bragg equation. The position of the peak gives the layer distance, while the shape of the peak gives information about the number of layers and the lateral extension.
In our laboratory we used a Seifert X-ray source with proportional and one-dimensional linear, multichannel detectors (MBraun). For in situ investigations a new shear cell was constructed by us.

Freeze-fracture method A small amount of the sample was solidified by liquid nitrogen, afterwards it was broken by a blade and a replica was formed on the fractured surface with platinum and carbon. Inserting the replica into an electron microscope, the morphology of the sample can be observed.

The freeze-fracture method was carried out in the Országos Baleseti és Sürgősségi Intézet (Budapest) by a Balzers BAF400D apparatus. Electron micrographs were taken by a Tesla BS 500 electron microscope.

DSC During the differential scanning calorimetry the temperature of the sample is varied according to a program and the enthalpy is registered. Thus the parameters of the phase transitions can be determined (temperature, temperature range and heat amount).
My DSC measurements were carried out in the Laboratory of Soft Matters of the Department, with a Setaram MicroDSC III calorimeter.

RESULTS

1. The construction of the rheoblock [1] The rheoblock is a small shear cell, which is mimicking the shear process occuring in oscillatory viscosimeters and can be used to study structural changes of the sample during shear. There are two versions, one for small angle X-ray scattering (SAXS) and an other for the freeze-fracture method. The frequency and the amplitude of the shear can be changed, the thickness of the sample is also variable. The sample holders can be thermally controlled (Fig. 1.).

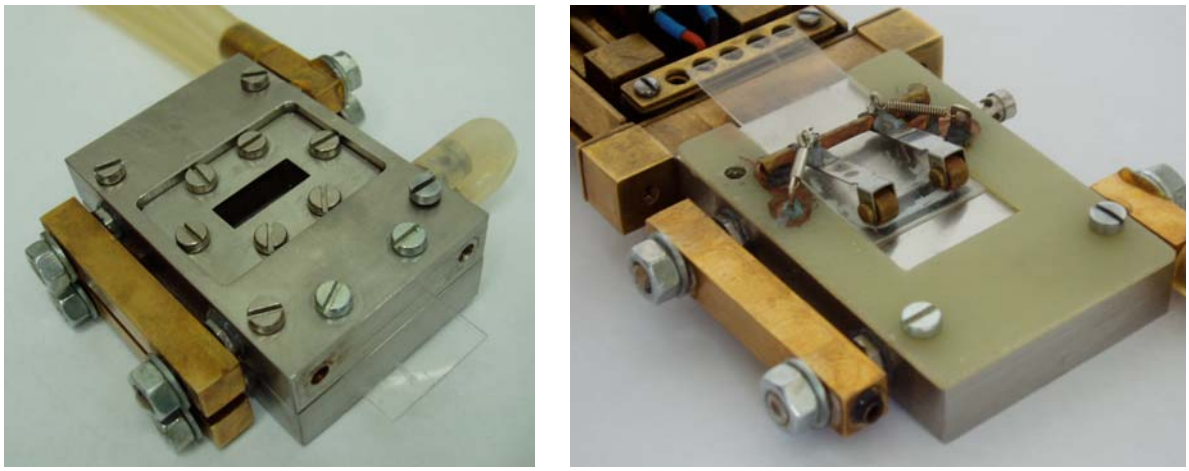
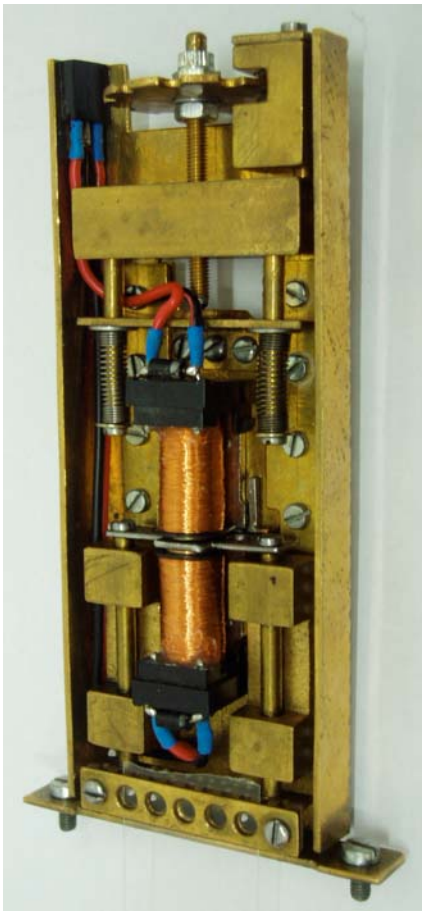


Figure 1. The sample holders of the rheoblock for SAXS and for freeze fracture

In the shear cell the sample is situated between two thin plastic sheets. One of them is fixed, the other one is moved up and down by the electromechanical mover and the digital control unit (Fig. 2.).



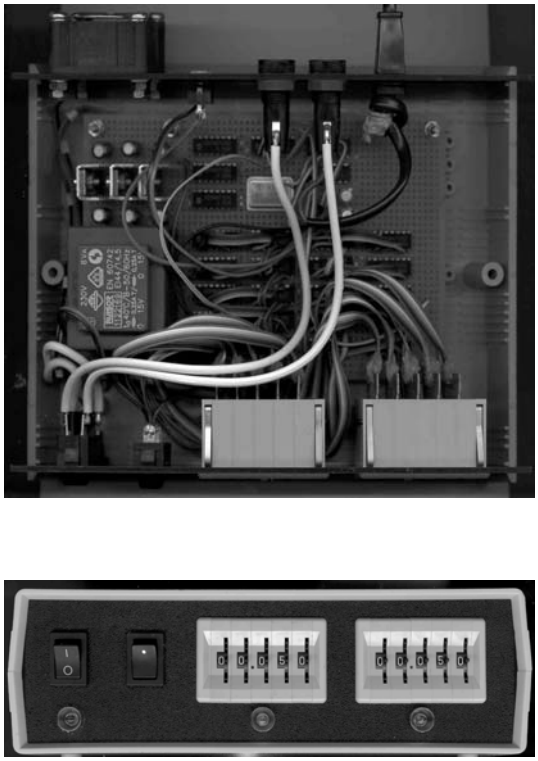


Figure 2. The electromechanical mover
and the digital control unit

2. Investigations at constant temperatures Applying a long-term shear to the 80% Synperonic A7-water system it was concluded, that the sample had a two-level structure: a layer structure with a layer distance of about 50 Å and a domain structure with a micrometer-scale extension (Fig. 3.). Comparing the freeze-fracture (Fig. 4.) and SAXS (Fig. 5.) results, it can be concluded, that the short-term shear affects only the domain formations and not the

Fig. 3.

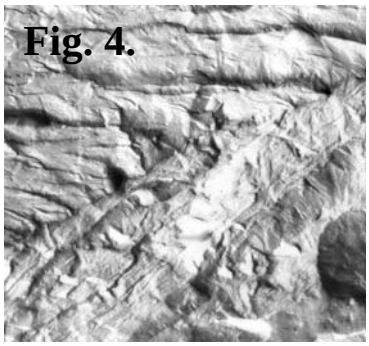


Fig. 4.

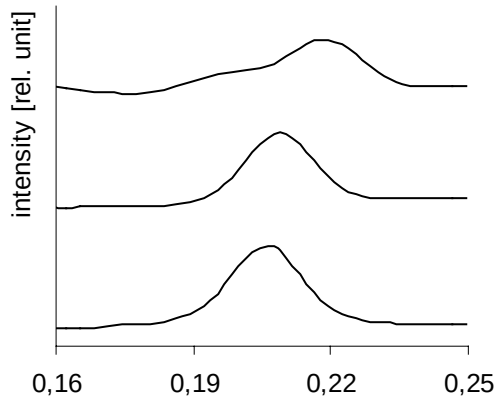


Fig. 5.

layer structure. It means that the fast viscosity decrease under shear and the tixotropic behaviour of the A7-water system originates rather from the changes of the domain structure than from the changes of the layer structure [2,3,4]. After some hours of shear phase separation occurs, which is explained by the formation of domains with different concentration of A7 [5]. It was supported by the investigation of samples with different concentrations.

At 60 °C, near to the temperature of the phase transition, the shear affects the layer structure much more significantly, it is destroyed in a relative short time (Fig 6.).

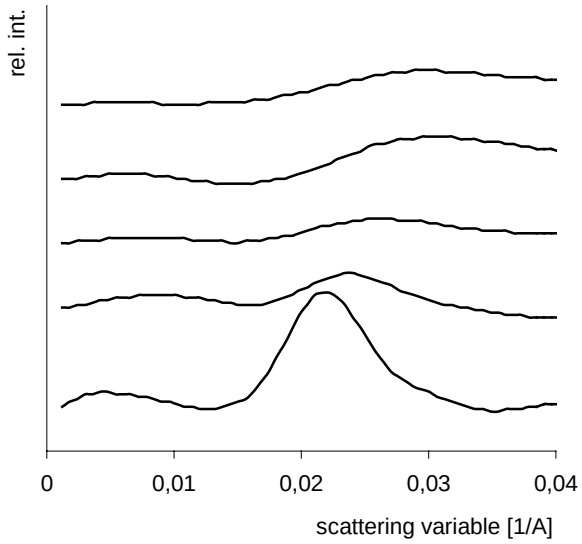


Fig. 6.

3. Combination of shear stress and thermal program [6,7]

During the thermal programs the 80% A7-water system was heated from 20 °C to 80 °C, then it was cooled down to 20 °C again. The gradient was 1 °C/min. Three different cases were studied: thermal program without shear; thermal program with continuous shear; and shear stress only at the heating period. In the first case the layer structure was destroyed by increasing temperature, but it was recovered in the cooling period (Fig. 7.). In the second case, when shear was applied to the sample, the heating caused approximately the same changes as previously, but in the cooling period no reapperance of the layer structure was observed (Fig. 8.). In the latter case the shear caused the the decomposition of the layer structure at a lower temperature. In the third case, when shear was applied only at heating, the layer structure was built up in the cooling period.

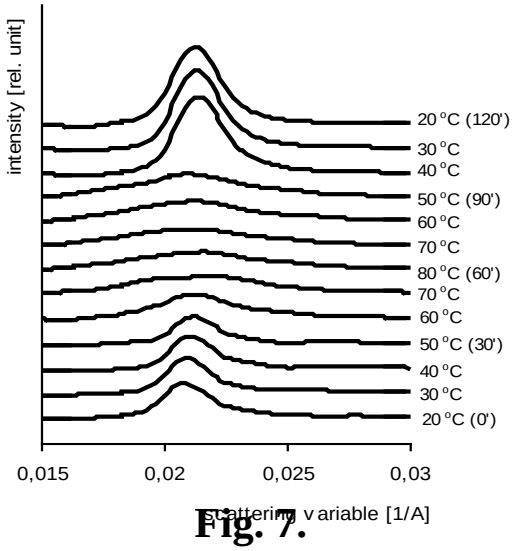


Fig. 7.

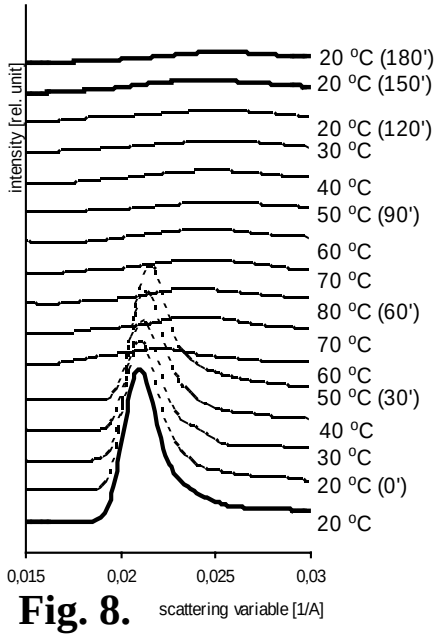


Fig. 8.

The first and second series of SAXS measurements were followed by freeze-fracture and no difference was observable in the electron micrographs of the 80 °C states: in both cases the remains of the layer structure were present in the sample (Fig. 9.). If shear is applied in the cooling period, further dissection of the domains occurs. The freeze-fracture images confirm the results obtained by SAXS.

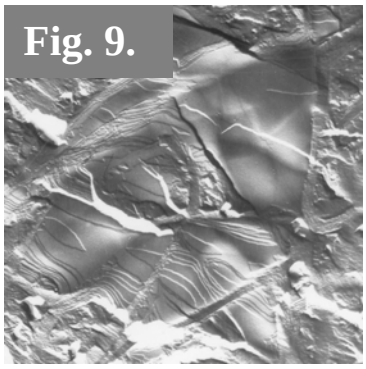


Fig. 9.

4. Thermoanalytical measurements After revealing the nanometer-scale and micrometer-scale structure of the 80% Synperonic A7-water system, DSC measurements were carried out to study the thermal features of the sample without shear and after shear. The effect of the shear is significant: the mechanical energy transmitted by the shear is collected in the sample and during the further treatment it transforms to thermal energy [8].

Samples with different concentrations were studied by DSC and it was concluded, that the presence of the remains of the layer structure above the temperature of the phase transition can be explained by the formation of domains with significantly lower A7 concentrations than 80% (Fig. 10.).

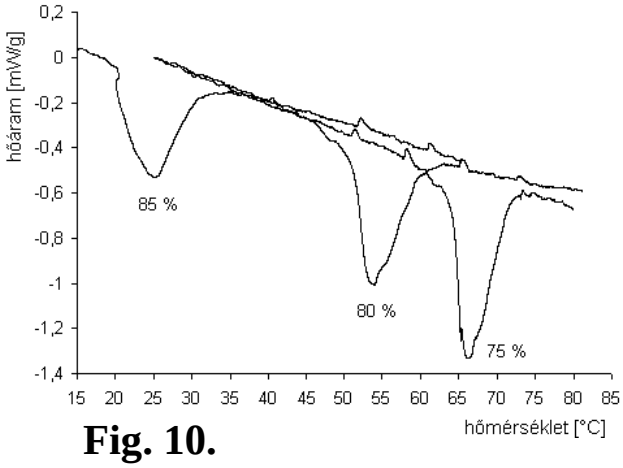


Fig. 10.

5. Investigation of a ferronematic liquid crystal Magnetite particles were dispersed in 8CB (4-cyano-4'-octyl-biphenyl) and a ferronematic liquid crystal was formed, which was investigated by freeze fracture. It was found, that the distribution of the magnetite particles is inhomogenuous. Homogenisation can be reached by shear stress, but in this case the lamellar structure of the liquid crystal becomes destroyed [9]. It suggests a general connection between the lamellar structure and shear stress.

APPLICATIONS

The majority of my work may be considered as a basic research, as I have been dealing with the structural changes of a simple two-component system under shear and thermal treatment. Since the system studied is a basic component of household chemicals and cosmetics, the application of my results has potential for future investigations.

My work demonstrates the fact, that studying microstructural systems needs the investigation of the whole colloid dimension.

It is probable, that my results, originating from the investigation of mostly one system, may be generally applicable on other lyotropic/lamellar systems. The results obtained from the studying the ferronematic liquid crystal also support this conclusion.

The rheoblock constructed by us is generally usable to carry out structural and morphological measurements with different systems (e.g. liposomes and complex systems of microemulsions).

PUBLICATIONS

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