PERIODICA POLYTECHNICA SER. CHEM. ENG. VOL. 48, NO. 1, PP. 3–12 (2004)

CONSTRUCTION OF A SHEAR CELL FOR SAXS AND FREEZE FRACTURE STUDIES

György FETTER and Attila BÓTA

Department of Physical Chemistry
and
HAS–BUTE Laboratory of Soft Matters
Budapest University of Technology and Economics
H–1521 Budapest, Hungary
Phone: (36 1) 463 2473
e-mail: gfetter@mail.bme.hu, abota@mail.bme.hu

Received: April 2, 2004

Abstract

Two variants of a sample holder were constructed for SAXS (small angle X-ray scattering) and freeze fracture studies of colloid systems during shear stress. The detailed construction of both variants is described. The SAXS investigations give information about the structural changes in the range of nm's, and the freeze fracture technique makes possible the imaging of the μm-scale morphology. Combining these methods the origin of certain macroscopical features, e.g. shear induced structural formations (like tixotropy) can be examined in a wide size range of the colloid dimensions.

Keywords: SAXS, freeze fracture, shear cell, layer structure, domain structure.

1. Introduction

The investigation and interpretation of the shear-induced structural formations have a great interest in the description of the rheological behaviour of number of systems existing in different fields of industry, like production of foods, detergents, pharmaceuticals [1]. Simultaneous scattering and rheological measurements are considered as powerful methods [2, 3], but the mutual correspondence of the results obtained by the two different kinds of methods is not unambiguous. The interpretation of the experimental data requires different assumptions expressed in different structural models. The rheological features are explained with shear induced structural changes occurring in the range of nm'sizes, while the structural formations in the range of the μm's are generally negligible. Therefore we intended to investigate the size range of μm by using the method of freeze fracture.

Our previous works revealed that the structure of a typical industrial surfactant-water system is drastically affected by shear [4, 5]. To obtain structural and visual information about the shear induced domain formation a shear cell was contstructed in two variants. The monitored size range extends from nm- up to μm-scales which can be detected by using small angle X-ray scattering (SAXS) and freeze fracture methods, respectively. Corresponding to this kinds of measurements, one variant

of the cell was built for the SAXS studies and another one for freeze-fracture [6, 7]. By this construction of the cell we had given up the measurements of the rheological data obtained by the conventional rotational- or oscilloviscosimetry, but a number of the shear parameters (shear rate, frequency, temperature of shear, thickness of sample) can be set and the shear process itself can be reproduced very precisely. However, the conditions of the shear process occurring in the constructed cell can be mimicked by an oscilloviscosimeter [7].

In this paper the technical description of both variants of the constructed cell is reported. To demonstrate the advantages of the shear cell we present some typical results obtained on the non-ionic surfactant/water (Synperonic A7-water) system. In this system the lamellar phase exists in the concentration range from about 50 up to 80 w/w %, between 10 and 60 °C. The system was already investigated very intensively with various methods [4]–[10]. It was found that its viscosity decreased extremely after some minutes of shear. The system exhibited tixotropy as the flow (shear stress as the function of the shear rate) and the viscosity curves were open: the value of the shear stress and the viscosity differed from their starting values. Using the two variants of the constructed cell we followed the changes occurred under shear and we could give an explanation for the tixotropy of the A7/water system.

2. The Construction of the Shear Cell

The shear cell constructed for SAXS is a sandwich-like one. This kind of cell geometry is already used by other research groups, too [11]. It consists of two rectangular bulks made of stainless steal with quadratic apertures in the centre of them for the transmission of the X-ray beam as it is shown in its technical scheme and photo in *Fig. 1a* and *1b*, respectively. The bulks are fastened together with screws. The sample is placed between two special, thin Plexiglas (PMMA) windows having minor SAXS. One of the windows is fixed; the other one is movable by the outer mover unit. The fixed window is set with a stainless steel frame in one of the bulks. The windows are set in the apertures of the bulks which have a height of 6 mm and a width of 16 mm. The thickness of the sample is adjustable with a convenient frame and its maximum value is 1 mm. The moving window is between the bulks and its free moving is assured by a Teflon (PTFE) sheet around it, which keeps the distance between the bulks.

The variation for freeze fracture uses one of the bulks with the fixed window, but instead of the other bulk there is a unit to press the alternating window to the same position that was placed in the other SAXS variant as it can be observed in *Figs. 2a,b*. This unit consists of two spring-pushed arms that keep the moving window in its working position through two rollers. Against the springs arms can be lifted up and in this position fast sampling is possible for the freeze fracture method. Incubation is carried out by water flow in both cases, through inner bores of the bulks.

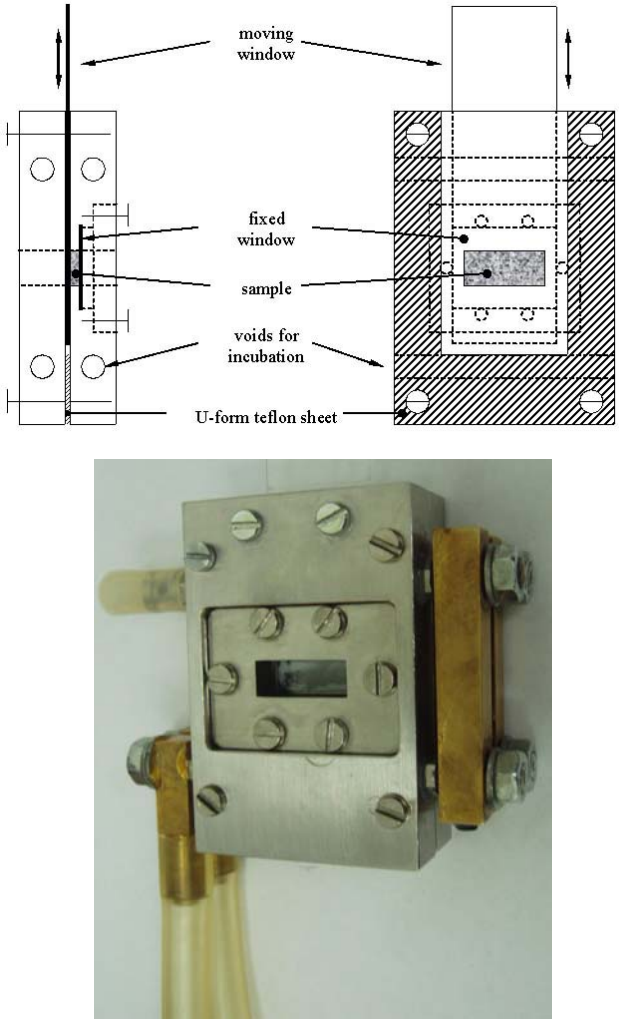

Fig. 1. The sample holder for SAXS

The electromechanical mover includes two solenoids with iron cores, which are alternately passed through by current and they draw a soft steel plate up and down. The construction of this unit is demonstrated in *Figs. 3a,b.* This alternating motion is forwarded by a track to the moving window. Changing the distance between the solenoids, increasing or decreasing of the shear amplitude can be achieved between 0 and 5 mm, the resolution is 0.05 mm.

The electronic unit driving the electromechanical mover is a double timer based on a crystal oscillator, switching voltage to the solenoids one after the other.

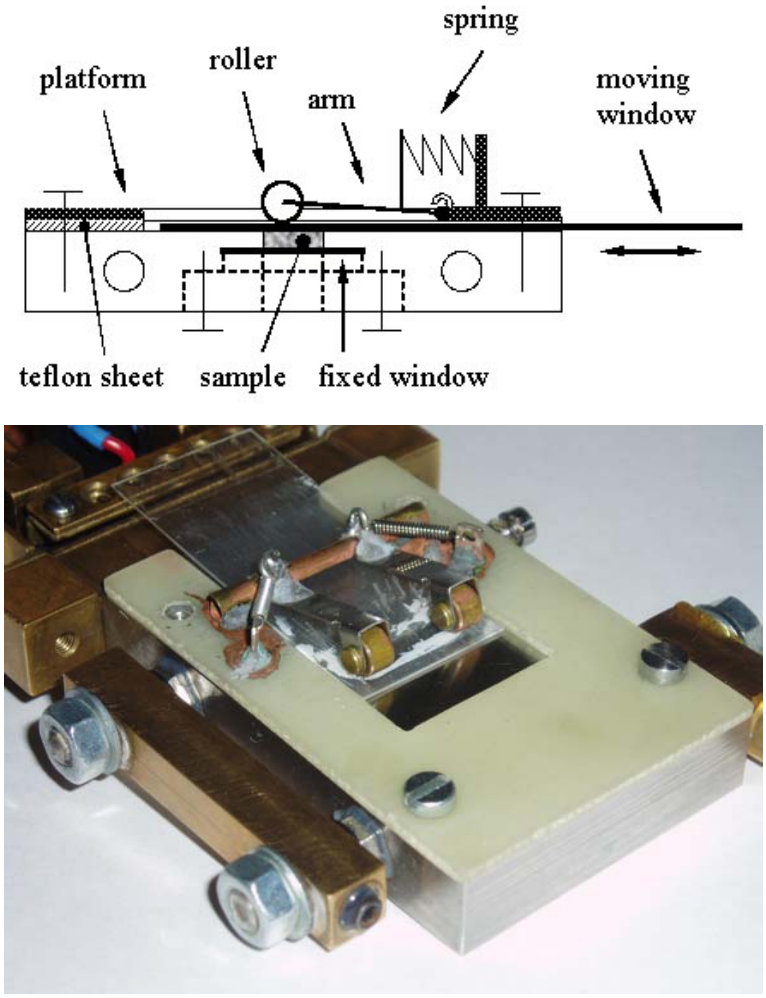

Fig. 2. The sample holder for freeze fracture

These time periods can be set separately by BCD (binary coded decimal) switches, the range is 0.001–100 s and the resolution is 0.001 s. The electronic unit permits triggered periodic movements (‘up’ and ‘down’) to occur with constant velocities and at the end positions the mechanic mover (and the window, too) is waiting for the time defined by the adjusted frequency. The path-time function of the moving window is a quadrangular sign. A drastic deformation of this sign function occurs at higher frequency. At the frequency of about 10 Hz, the mowing window is always moving ‘up’ and ‘down’ (there is no more waiting at the end positions) and its path-time function becomes to a nearly sinusoidal form. That is the reason why the condition of the shear cell by can be mimicked an oscilloviscosimeter. At higher

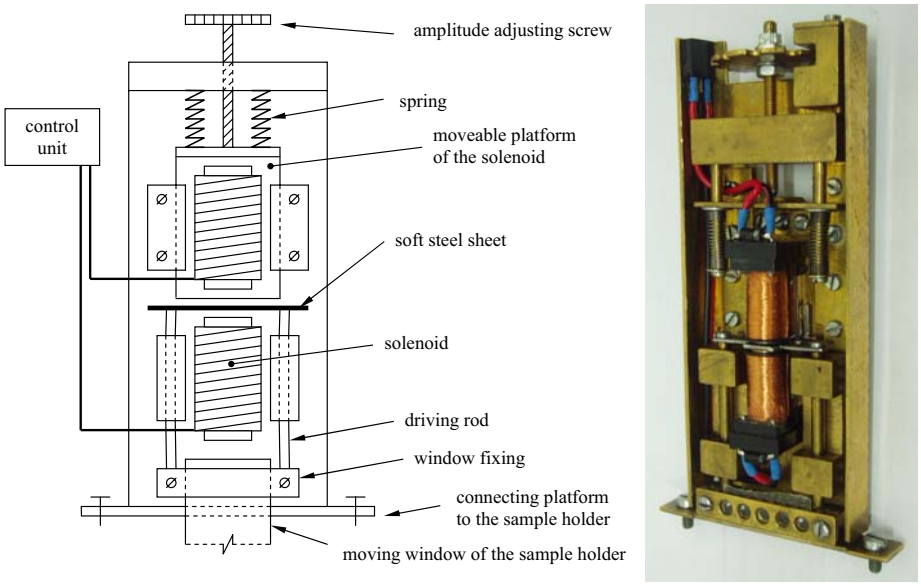

Fig. 3. The electromechanic mover

frequency (about 20–30 Hz) the mechanical unit is not able to follow the digital unit and non-periodic movement occurs. The shear rate was calculated from the amplitude of the movement (adjusted with an error range of about 2%), the periodic time (measured electronically) and the width of the sample. The shear rate was adjusted for a constant maximal value (at crossing the time axe, about 8 1/s) during both of the two kinds of measurements, e.e. SAXS and freeze-fracture.

3. Experimental

3.1. Materials

The Synperonic A7 is an ethoxylated fatty alcohol with C_{13} and C_{15} alkyl chains and with an average ethoxylation number of 7 (but this number is between 0 and 15 in the product of ICI Surfactants, Brussels, B). The tenside was used as supplied, it was mixed with 20% distilled water, heated up to 60 °C and stirred for 30 min. then ultracentrifuged to yield a bubble-free material and finally left at 20°C for 1 week.

4. Methods

A modified compact Kratky camera (Anton Paar, Graz, Austria) supplied with a linear, one dimensional position-sensitive device (Mbraun, Garching, Germany)

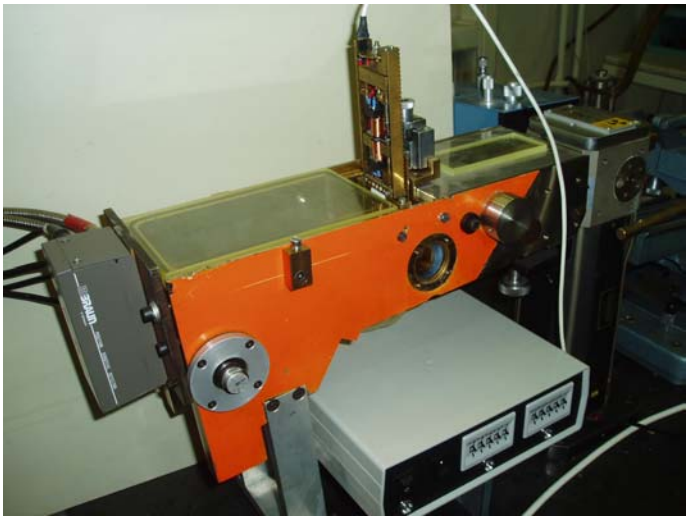

Fig. 4. The modified Kratky camera with the shear cell

was used to record the SAXS patterns which allowed relatively short exposition times (1–2 minutes). The source was a Ni-filtered Cu K_α radiation ($\lambda = 1.542$ Å). The Kratky camera had a unified inner space because of the vacuum needed for the measurements, thus it had to be modified to be able to accommodate the shear cell. An open section was formed in the middle of the camera for the shear cell. The complete measurement apparatus, the SAXS camera with the shear cell and the electronic unit can be seen in the *Fig. 4*.

The freeze-fracture technique was used as usual. The gold specimen holders were preincubated at the same temperatures as the block of the shear cell. Samples in small volume (of about 1–2 μl) were taken out under the flexible window of the shear cell by using a fine palette-knife and were placed onto the gold holders, which were then immediately plunged into partially solidified Freon for 20 s freezing and than placed and stored in liquid nitrogen. Fracturing was carried out at $-100\,^\circ$C in a Balzers Freeze-Fracture Device (Balzers AG, Liechtenstein). The fractured faces were etched for 30 s at $-110\,^\circ$C. The replicas, prepared by platinum-carbon shadowing, were cleaned with a solution of hypochlorous acid and washed with distilled water. From pure water, the replicas were picked up on 200 mesh copper grids. The electron micrographs were taken with an electron microscope (Jeol JEM-100 CX II, Japan).

5. Results

The Synperonic A7-water system (80 w/w%, 20 °C) has a characteristic SAXS pattern having two Bragg reflections. The first Bragg reflection is relatively sharp

corresponding to a well ordered layer structure, while the second one is very small. The displacement of the Bragg peak informs about the mean periodic distance by a single relation, namely $d = 1/s_{max}$, where s_{max} is the value of the scattering variable (s, defined as $s = (2/\lambda) \sin \Theta$, where Θ is the half of the scattering angle), which is at the maximum of the Bragg reflection. Within the curvatures only the shapes of the Bragg peaks were influenced by shear, therefore only the Bragg profiles were detected as a function of the shear time, as shown in *Fig. 5*. The shapes as a function of the Bragg peak did not change significantly with shear. After 2 hours of shear the layer distance was shifted from the starting value of 48.3 Å to 46.8 Å. After 3 hours the layer distance decreased slightly to 46.5 Å while the intensity of the reflection was increased to about 1.5 times higher than it had been in the starting state. The latter change indicated that the lamellar arrangement was more typical for the whole sample after shear than in the starting steady state. After the end of shear the profile of the peak was broadened corresponding to a less ordered layer structure. In the shear cell the changes of the thermotropic behaviour can also be followed as presented in the case of the same A7-water system detected at 60°C (*Fig. 6*). At 60 °C in steady state only very broadened Bragg reflection appeared indicating that the lamellar arrangement was destroyed drastically due to the higher thermal fluctuations. After 10 minutes of shear the peak was decreased significantly and after 1 hour shear it practically disappeared.

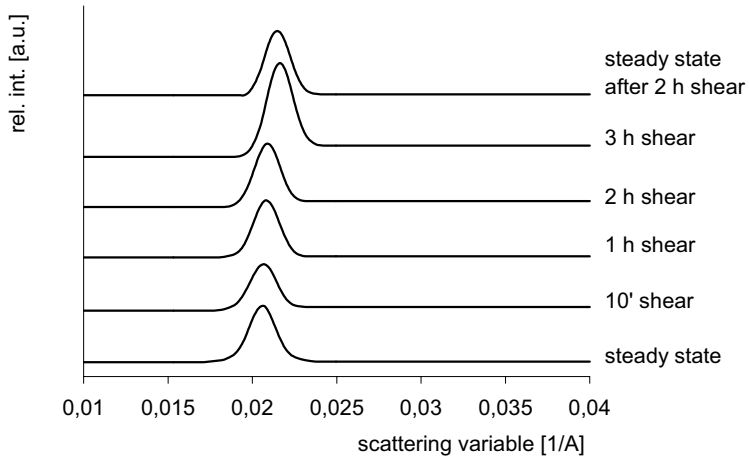

Fig. 5. SAXS patterns during shear at 20 °C

Freeze fracture images exhibited the evidence of a well ordered layer arrangement of the steady state in full agreement with the SAXS measurement. The typical pictures showed closely packed parallel layers with smooth surface as it can be observed in *Fig. 7*. However, unregular stacks and other defects appeared occasionally. It was obvious, that the stacks of the parallel layers were distributed randomly and no macroscopic orientation existed, therefore we can conclude that the profile of

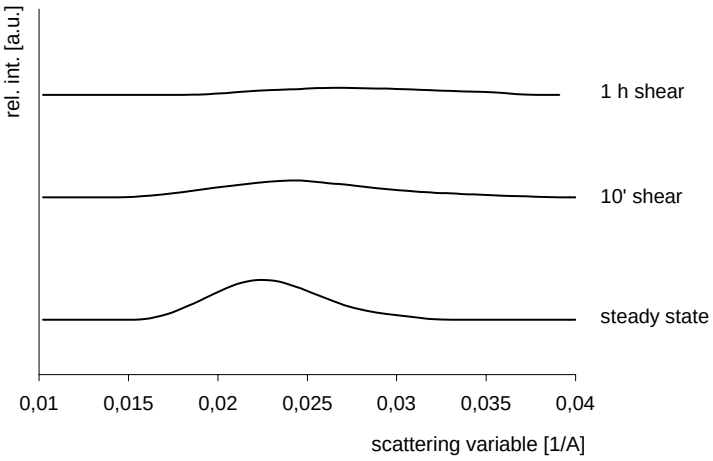

Fig. 6. 6 SAXS patterns during shear at 60 °C

the Bragg peak is a consequence of a not oriented, 'powder sample' structure. After 5 minutes of shear the sample became dissected, the large sheets of layers are considerably broken, but a significant part of the sample was still unchanged as demonstrated in *Fig. 8*. After 2 hours of shear the sample was totally dissected, large sheets did not exist as shown in *Fig. 9*. The homogeneous parts of the sample were broken down into smaller domains with a maximal extension of about 0.5 μm. The pictures of the freeze-fracture revealed that aggregates with larger sizes (up to several μm) also existed. It must be stressed out that the elementary lamellar arrangement was always present, but the number of sheets and their lateral extension were reduced extremely. However, this domain size of the lateral extension proved to be enough to exhibit significant Bragg reflection. Consequently, we can suppose higher layer correlations inside of the stacks after the shear than before shear.

6. Conclusion

The simultaneous SAXS and freeze fracture studies revealed that the nm-scale layer structure and the μm-scale domain structure of the Synperonic A7-water system (80 w/w %) were influenced by shear. Applying shear stress, considerable changes occurred in the domain structure in a short time, while the layer structure was nearly constant during a long period of shear. It means that the short-term alteration of the rheological behaviour during shear was caused mostly by the changes of the domain structure and not of the layer structure.

The two variants of the shear cells constructed proved to be a powerful method to reveal the structural and morphological changes induced by shear.

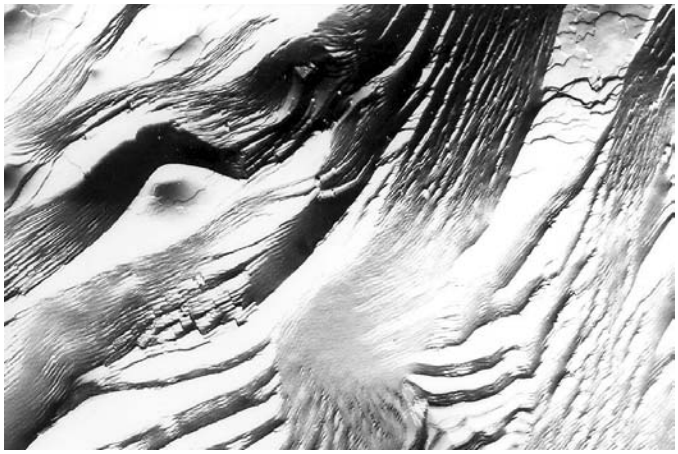

Fig. 7. Freeze fracture image in steady state at 20 °C (The width of the picture represents a bar of 9 μm.)

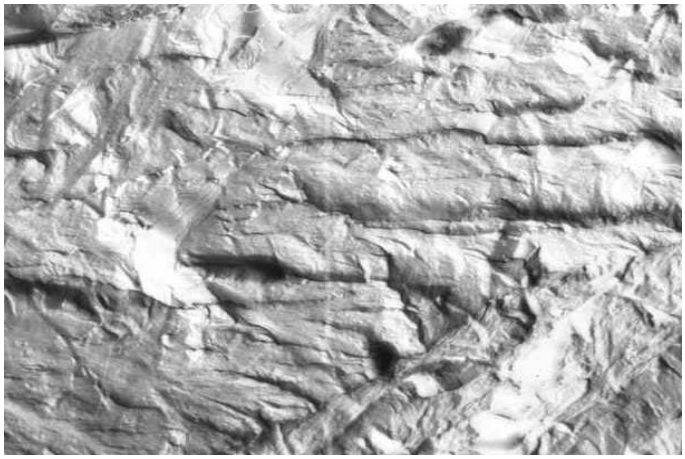

Fig. 8. Freeze fracture image after 5 minutes of shear at 20 °C (The width of the picture represents a bar of 9 μm.)

Acknowledgements

We thank to Ms. T. Kiss (Budapest,H) for the technical assistance at the freeze-fracture technique. This work was supported by the Hungarian Scientific Funds OTKA (Bota, T 21781, T 43055) and a bilateral German-Hungarian Program TÉT (D-42/1998).

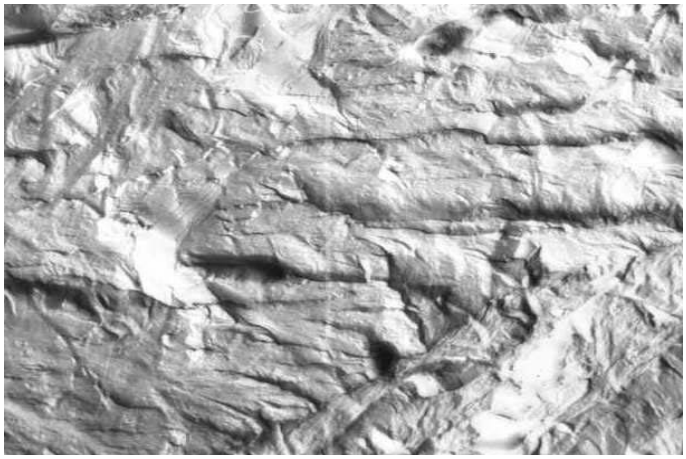

Fig. 9. Freeze fracture image after 2 hours of shear at 20 °C (The width of the picture represents a bar of 9 μm.)

References

[1] MCHICK, M. J. Ed., *Nonionic Surfactants, Physical Chemistry: Surfactant Science Series*; Marcel Dekker: New York, 1987.
[2] PENFOLD, J. – STAPLES, E. – KHAN LODHI, A. – TUCKER, I. – TIDDY, G. J. T., *Phys. Chem. B.* **101** (1997), p. 66.
[3] MANG, J. T. – KUMAR, S. – HAMMOUNDA, B., *Euro Phys. Lett.* **28** (1994), p. 489.
[4] NÉMETH, ZS. – HALÁSZ, L. – PÁLINKÁS, J. – BÓTA, A. – HORÁNYI, T., *Colloid and Surfaces A.* **145** (1998), p. 7.
[5] HALÁSZ, L. – NÉMETH, ZS. – PÁLINKÁS, J. – HORÁNYI, T. – BÓTA, A., *Progr. Colloid Polym. Sci.*, **117** (2001), p. 159.
[6] FETTER, GY. – HORÁNYI, T. – BÓTA, A., *Progr. Colloid Polym. Sci.*, **117** (2001), p. 217.
[7] BÓTA, A. – FETTER, GY., *Langmuir* (2004) in press.
[8] DIMITROVA, G. T. – TADROS, TH. F. – LUCKHAM, P. F. – KIPPS, M. R., *Langmuir* **5** (1996), p. 315.
[9] TADROS, TH. F. – DIMITROVA, G. T. – LUCKHAM, P. – FTAELMAN, M. C. – LOLL, P., *Euro Cosmetics* **3** (1995), p. 17.
[10] DIMITROVA, G. T. – TADROS, TH. F. – LUCKHAM, P., *Langmuir* **11** (1995), p. 1101.
[11] HAMLEY, I. W. – POPLE, J. A. – GLEESON, A. J. – KOMANSCHEK, B. U. – TOWNS-ANDREWS, E., *J. Appl. Cryst.*, **31** (1998), pp. 881–889.