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SHEAR EFFECT ON THE THERMOTROPIC BEHAVIOUR OF THE SYNPERONIC A7–WATER SYSTEM

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The thermotropic behaviour of the Synperonic A7–water (80%) system was investigated by different (SAXS, freeze-fracture, DSC) methods under the conditions of steady state and shear stress. It was found that above the melting point (about 55°C) lamellar structure exists at 80°C, which was interpreted as a consequence of phase separation. The phase separation is more extended if the sample was sheared. The shear process affects the thermotropic behaviour of the system drastically. Above the melting point the thermal treatment terminates the shear prehistory. The shear processes were executed in a shear cell constructed in two variants for small angle X-ray scattering and for freeze-fracture methods.

Keywords: *layer structure, shear-induced defect, surfactant, Synperonic A7*

Introduction

Among the different surfactants the Synperonic A7 is frequently studied because it is a basic precursor for a number of washing-materials and cosmetic products [1]. Dispersing the nonionic surfactant Synperonic A7 in water enables the formation of different (liquid with normal micelles, hexagonal, lamellar, liquid (with inverse micelles)) liotropic structures [2]. The lamellar phase exists in the concentration range from about 50 up to 85 mass/mass%. The rheological features of the lamellar phase were studied intensively and concluded that the system is tixotropic [3–5]. To reveal and characterize the tixotropic behaviour, the simultaneous application of scattering and rheological methods proved to be effective [6].

We have constructed a shear cell for the study of the structural changes occurring during the shear stress [7]. The shear cell constructed in two variants enables small angle X-ray measurements and freeze-fracture investigations, too. Using this cell we have concluded that the tixotropic behaviour originates from the domain formations extended in the scale of μm-s and it hardly depends on the changes of the characteristic layer structure [8]. The calorimetric methods serve very valuable information about the features of colloidal systems [9], consequently the DSC method was used to reveal the the termotropic effect of the shear process. After long shear stress at constant temperature (20°C) the domains render with different Synperonic concentration as it was observed by small angle X-ray scattering (SAXS) method [10]. Following the structural and morphological changes in an extended temperature interval from 20 up to 80°C a phase separation appears which can be observed by freeze-fracture method directly and explained by the thermotropic features of the system described in the present work.

Experimental

Materials and methods

Synperonic A7 is an ethoxylated mixture of C13 and C15 1-alcanols with an average ethoxylation number of 7.3. Synperonic A7 solution (80 mass/mass%) was made with distilled water, stirred for 30 min at 60°C and then ultracentrifuged to be bubble-free. The grease-like sample was stored at room temperature for one week.

The shear cell fixed in a small angle X-ray camera enables observations of the changes of the lamellar structure (or of other kinds of nanoscale structures), while using the shear cell on a freeze-fracture device provides direct visualisation of the morphology affected by shear. The shear conditions induced by the cell and by the rheometers used are generally different, but the conditions of the cell constructed can be mimicked by an oscillatory rheometer [9].

The sample holder consists of two windows and a stainless steel frame. One of the two windows is moved ‘up and down’ periodically with a maximum shear rate of 8 s^{-1} (adjusted typically at 10 Hz). The block of the sample holder can be incubated. The construction of the cell allows SAXS measurements with transmission geometry, while the shear cell variant constructed for freeze-fracture has a flexible fastening of the moving window, which assures fast sam-

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pling. The full technical description of the two variants is already summarized in an another paper [7]. The windows of the sample holder are made of a special Plexiglas which have a minor effect on the SAXS.

The SAXS measurements were performed by a modified compact Kratky camera (Anton Paar, Graz, Austria) supplied with a linear one-dimensional position-sensitive detector (MBraun, Garching, Germany). The intensity of the Ni-filtered CuK_α radiation (λ=0.1542 nm) was recorded in the 10^{-2} – 1 nm^{-1} range of the scattering variable, defined as $s=(2\sin\Theta)/\lambda$, where 2Θ is the scattering angle. The primary beam was slit-collimated. The intensity curves were corrected by considering the geometry of the beam profile in order to obtain point-focused curves.

In the freeze-fracture method samples of small volumes (about 1–2 μL) were gently 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 resulting in freezing and then placed and stored in liquid nitrogen. Fracturing was carried out at –100°C in a Balzers freeze-fracture device (Balzers AG, Liechtenstein). The fractured faces were etched for 30 s at –110°C. The replicas, prepared by platinum-carbon shadowing, were cleaned with distilled water. The electron micrographs were taken by an electron microscope (Jeol JEM-100 CX II, Japan).

The calorimetric scans were performed by using a special micro DSC III instrument (SETARAM, France) operating at a scan rate of 0.25 K min^{-1} in the temperature range from 5 up to 80°C. The reference vessel was empty. The DSC curves were recorded in the heating and cooling directions in all cases. The temperature at the peak maximum was defined as the transition temperature. The calibration of the calorimeter was carried out by using a pure naphthalene sample (T_{onset}=80.3°C). The standard 'batch' vessel is composed of a cylinder of 6.4 mm of internal diameter and a useful height equivalent to 19.5 mm for the sample. The useful volume for the sample is equal to 1 cm^3.

Results

The Synperonic A7-water (80 mass/mass %) system exhibits a phase-transition between the lamellar and the liquid structures around 54°C with a large temperature interval from about 45 until 60°C. The characteristic DSC peak does not depend on the scan rate (used 1, 0.5, 0.25, 0.02°C min^{-1}) indicating that the relaxation processes are fast. The DSC peak is slightly deformed in the case of the cooling scan and it shows a complex character of the transition process. However, the phase transition is reversible in the sense that the transition point appears at nearly the same temperature value during the heating and cooling scans. The DSC measurements are reproducible as it is demonstrated by the three DSC curves in the Fig. 1. The average change in enthalpy is about 1.00±0.01 J g^{-1}. The characteristic morphologies of these phases can directly be observed by using freeze-fracture methods. The fractured surfaces of the system obtained after quenching from 20 and 80°C show the features of the lamellar and the liquid phases, respectively. The lamellar phase exhibits large domains of stacks with parallel arrangements, while the characteristic morphology of the liquid phase is more 'melted-like' as it can be compared in the Figs 2a, b. Surprisingly, domains with lamellar arrangement appear in the electronmicrographs taken on the liquid phase at 80°C.

The existence of the lamellar structure at 80°C (at significantly higher temperature than the melting point of the 80% Synperonic A7–water system) originates from the inhomogeneous surfactant concentration as it was concluded after the study of the systems having 75, 80 and 85% surfactant concentration. The systems perform different thermograms shown in Figs 3a, b. The system with 75% concentration exhibits significantly higher and the other one with 85% exhibits significantly lower transition point than the reference sample with 80%. This observation corresponds to the schematic phase diagram of the Synperonic A7-water system, which renders a nega-

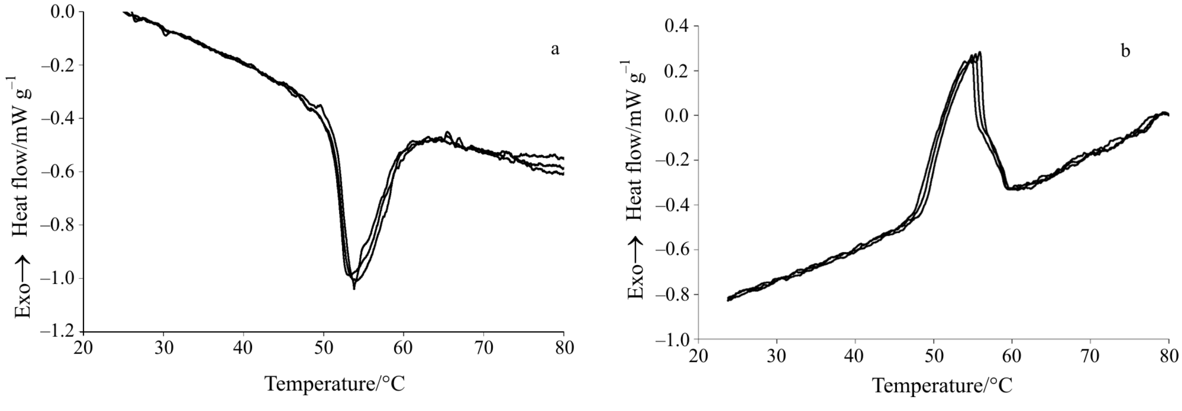

Fig. 1 DSC curves of the Synperonic A7-water system obtained after three measurements; heating scan (a – 0.25°C min^{-1}), cooling scan (b – 0.25°C min^{-1})

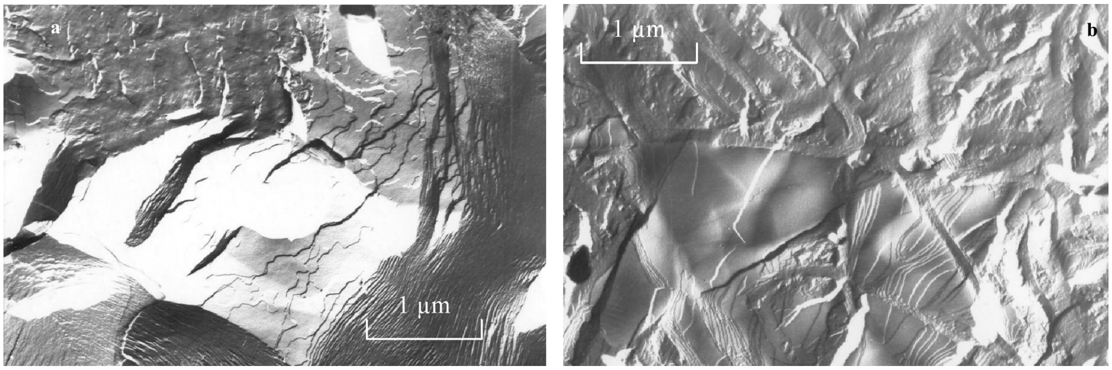

Fig. 2 The characteristic surface morphology of the Synperonic A7-water system in steady state; a – lamellar arrangement at 20°C and b – 'melted-like' state at 80°C

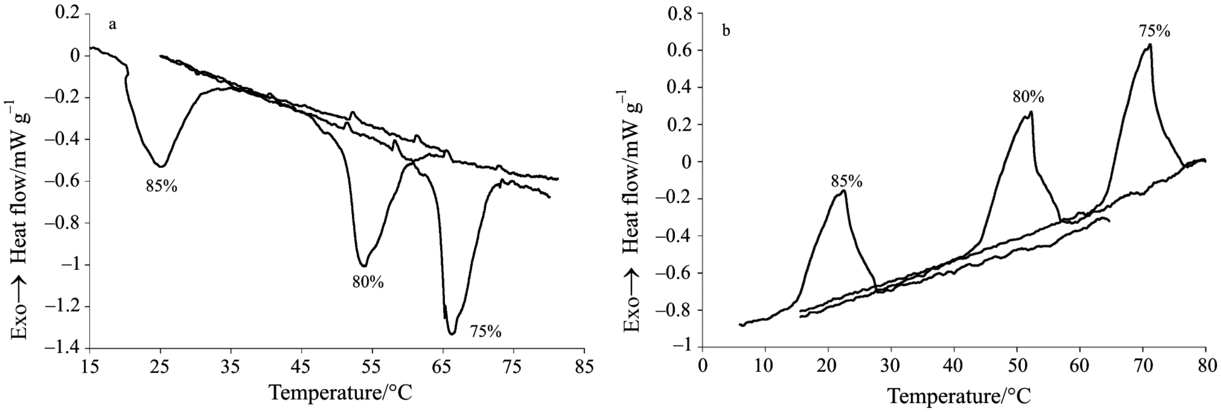

Fig. 3 DSC curves of the Synperonic A7-water systems (75, 80 and 85 mass/mass% Synperonic A7 with 0.25°C min^{-1} scan rate; a – heating scan; b – cooling scan

tive slope of the curve between the lamellar and reverse micelles phases.

The lamellar structure of the system was significantly affected by shear as it can be seen in Fig. 4. The structural change was monitored by SAXS on the sheared sample during a heating process executed with 1°C min^{-1} scan rate. The shape of the Bragg profile is characteristic for any kind of change in the lamellar arrangement. Under the melting point (54°C) the Bragg peaks are relatively sharp indicating a well-ordered layer structure. The position of the Bragg peak gives the periodic distance of the lamellar arrangement (by the $d=1/s_{\max}$ relation, where $s_{\max}$ is the scattering variable at the peak maximum). The average periodicity of the system is 4.83 nm. At 60°C the peak profile becomes to be diffuse corresponding to the melting process, but above this temperature the peak is not disappeared entirely, in spite of the fact that the system is in the temperature domain of the liquid phase.

The broadened peak profiles can be interpreted as the sum of several peaks belonging to different layer periodicities, but the position of the diffuse peak indicates an average layer distance of about 4.5 nm. The complex character of the Bragg profile shows that the structure of the sample is inhomogeneous. The same change in the Bragg profile was observed under the melting point at 20°C after long shear stress, where the periodicities were fitted to 4.59 and 5.07 nm [9].

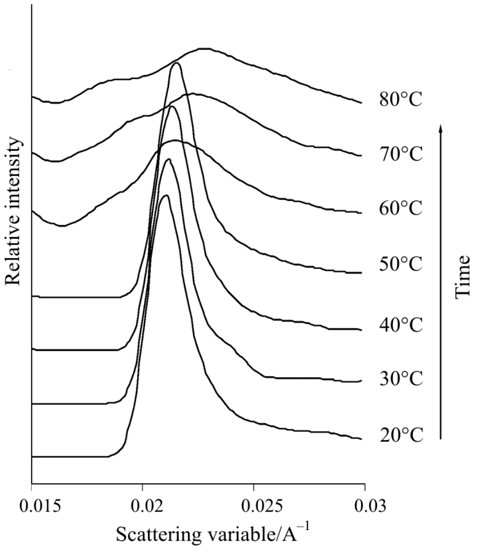

Fig. 4 Changes of the Bragg profile of the Synperonic A7–water system under shear as function of the temperature

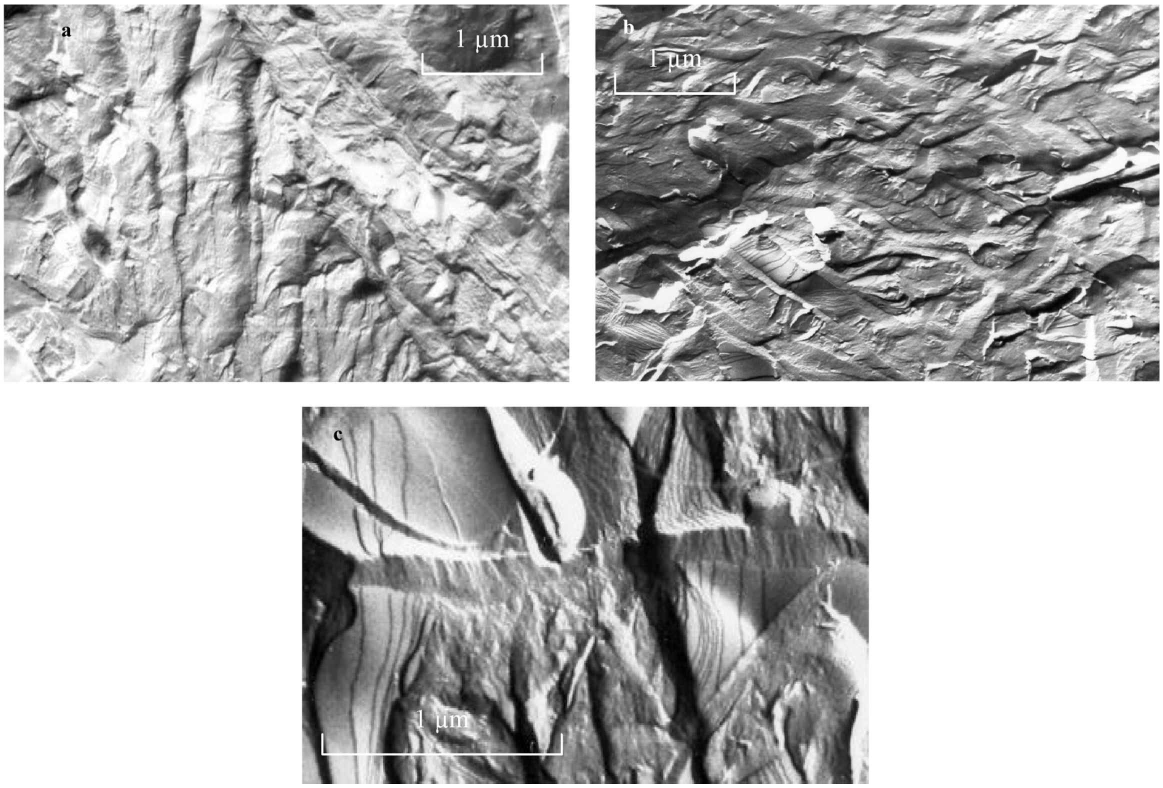

Fig. 5 Freeze-fracture electronmicrographs of the Synperonic A7-water system during shear: a – after 5 min of shear at 20°C; b – at 80°C and c – cooling down to 20°C

Nearly the same periodicities can be found for the systems having 75 and 85% Synperonic A7 (at 20°C, without any shear), consequently the shift of the average periodic distance (from 4.8 to 4.5 nm) indicates that the system has lamellar domains having significantly smaller surfactant concentration than 80%. The appearance of the domains with different periodicities indicates a separation in the sample. At the same time the broadened peaks show that the sample is dissected into significantly smaller domains than the ones exist in the starting state without any shear, therefore we can conclude that the sample consists of small domains with different periodicities.

In the shear cell constructed for the freeze-fracture the same shear processes were executed as during the SAXS measurements. The freeze-fracture procedures were made under shear at 20 and 80°C (the starting and the final states of the heating scan, corresponding to the lower and upper Bragg profiles in Fig. 4). Observing the pictures obtained on the freeze-fracture surfaces it is obvious that the shear significantly affects the structure. The large sheets with layer arrangements are dissected already after a 5 min of shear stress as it can be seen in Fig. 5a. The elementary domains become to be small with sharp squared up boundaries and they are long-shaped. Heat-

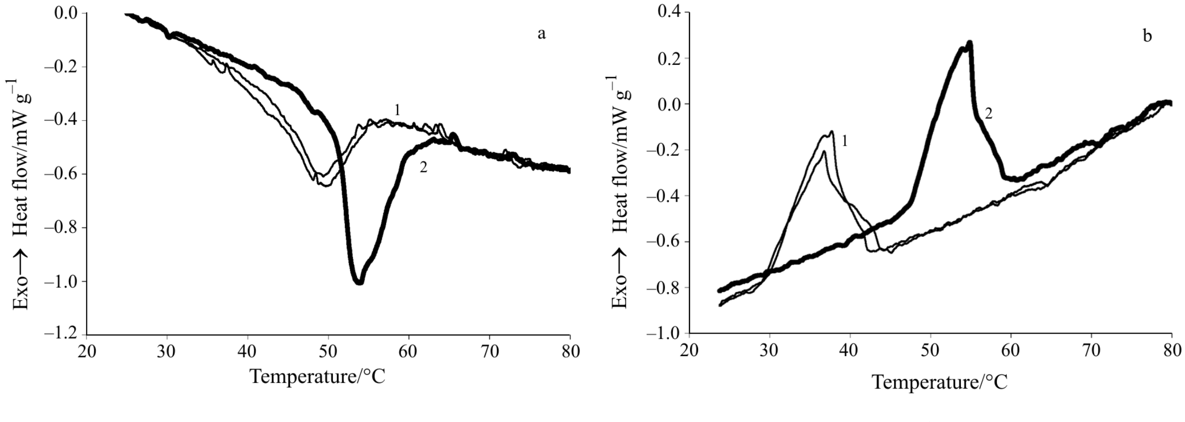

Fig. 6 The effect of the shear on the DSC curves of the Synperonic A7-water systems (0.25°C min^{-1} scan rate, 1 – sheared; 2 – steady states), a – heating scan, b – cooling scan

ing up the sample to 80°C, the surface morphology remains towards dissected but it becomes 'melted-like' and the same as it was observed without any shear (Fig. 5b). Under closer inspection we can also observe domains with lamellar structure (Fig. 5c).

The effect of the shear on the thermotropic behaviour was directly observed in the calorimeter (Figs 6a and b). The Synperonic A7–water (80 mass/mass%) system was sheared permanently during one hour. The sheared sample was filled into the DSC sample holder. The DSC curves indicate strong shear prehistory in both heating and cooling scans. The melting point is at about 49°C in the heating scan and at about 37°C in the cooling scan. The average change in enthalpy is 0.62 ± 0.07 J g^{-1} in the heating direction and it is 0.98 ± 0.03 J g^{-1} in the cooling direction. The latter value corresponds to that of the case without any shear.

Conclusions

During the heating processes domains are spontaneously formed with different surfactant concentration and the domains having significantly smaller concentration than 80%, remain in lamellar phase above the characteristic melting point of the system. Three different methods (calorimetry, X-ray scattering and freeze-fracture) reveal that the characteristic structure of the Synperonic A7–water system (80%) is strongly affected by shear and the domain formations become more complex and all kinds of the defect structures are present. The defect structures may conserve the mechanical energy introduced by the shear process, therefore a smaller value in the melting enthalpy appears during the heating scan. The effect of the accumulated energy can cause the strong decrease in the transition point and the inner relaxation processes also influence this characteristic point in the heating and cooling directions, as well.

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