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Disconnected lamellar phases (L_α) in pseudobinary water–non-ionic surfactant systems: A general phenomenon ☆

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Abstract

This study provides new experimental evidence for the disconnection of the lamellar phase (L_α) in pseudobinary water–non-ionic surfactant systems. To prove that the disconnection is indeed a general phenomenon the phase behavior of the pseudobinary system water–pentaethylene glycol dodecyl ether/hexaethylene glycol dodecyl ether (H_2O–$C_{12}E_5$/$C_{12}E_6$) was investigated as a function of the surfactant composition δ and the total surfactant concentration γ. At a fixed γ of 0.10 the extension of the highly diluted L_α phase shrank continuously with increasing amount of $C_{12}E_6$, i.e., increasing δ, until it disappeared at $\delta = 0.60$. The γ–T phase diagram of this particular surfactant mixture was found to have a disconnected L_α phase. For the first time, SAXS measurements were carried out to monitor structural changes related to the disconnection. For this purpose the interlayer spacing d and the effective cross-sectional area a_s were determined from the SAXS data along characteristic paths through the L_α phase.

Keywords: Non-ionic surfactants; Phase diagram; Lyotropic liquid crystals; Dilute lamellar phase; Disconnected lamellar phase; SAXS

1. Introduction

Binary mixtures of water and non-ionic surfactants can self-assemble into a variety of structures. By simply changing the concentration and the temperature one can observe the formation of spherical and cylindrical micelles, lyotropic liquid crystals (cubic, hexagonal, and lamellar), sponge type structures, and vesicles [1–5]. The focus of the study at hand is on two striking features of the lamellar phase (L_α), namely the occurrence of highly diluted and disconnected L_α phases, respectively, which will be described in the following.

Only about 15 years ago the L_α phase of the binary system water–$C_{12}E_5$ (pentaethylene glycol dodecyl ether) was found to swell to approximately 99 wt% of water [6]. This was a surprise since $C_{12}E_5$ is a non-ionic surfactant, i.e., that stabilizing electrostatic forces are lacking, and a formation of a structured phase at surfactant concentrations as low as 1 wt% was not expected. Indeed, dilute lamellar phases in binary water–non-ionic surfactant systems turned out to be a special feature of a small numbers of surfactants only, namely $C_{12}E_5$ [6], $C_{12}E_4$ [7], $C_{10}E_4$ [8], $C_{10}E_3$ [9], and three surfactants, the hydrophobic parts of which are branched [10,11]. The influence of the molecular structure on the absence or presence of the dilute L_α phase can be demonstrated very well with the phase diagrams of binary water–$C_{12}E_j$ systems. Whereas $C_{12}E_4$ and $C_{12}E_5$ form highly diluted L_α phases down to concentrations of 1 wt% ($C_{12}E_5$) or even less ($C_{12}E_4$), the phase diagram of $C_{12}E_6$ exhibits an L_α phase only at concentrations higher than 60 wt% [12,13]. On the other hand, the decrease of the alkyl chain length from C_{12} to C_{10} can have the same effect as an increase of the hydrophilic head group, namely a suppression

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☆ The research project reported in the paper at hand started in July 2005 during a visit of C.S. in the group of Prof. Hironobu Kunieda. Prof. Kunieda was very anxious to show that the disconnected lamellar phase is a general phenomenon. Unfortunately, he passed away totally unexpectedly in November 2005 before the project was finalized. Thus the present manuscript is dedicated to Prof. Kunieda and his never-ending interest in Phase Science.

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of the diluted part of the L_α phase. This tendency can be seen quite clearly when the phase behavior of $C_{12}E_5$ and $C_{10}E_5$ is compared. For the former the L_α phase extends from surfactant concentrations of about 90 wt% down to 1 wt% [6], whereas for the latter an L_α phase is only observed from 70 to 80 wt% [14]. Thus, starting from $C_{12}E_5$, a decrease of the alkyl chain length by two carbon atoms (from $C_{12}E_5$ to $C_{10}E_5$) as well as an increase of the head group length by one $–CH_2CH_2O–$ unit (from $C_{12}E_5$ to $C_{12}E_6$) drastically changes the phase behavior, i.e., completely suppresses the dilute L_α phase. In other words, for a given alkyl chain a decrease of the head group length and for a given head group an increase of the alkyl chain lead to the formation of a dilute L_α phase.

While highly diluted L_α phases were not discovered until 15 years ago, it was only about 6 years ago that the formation of a disconnected L_α phase in water–non-ionic surfactant systems was reported [15–17]. Wagner and Strey [15] found that the surfactant $(CH_3)_3Si(CH_2)_6(OCH_2CH_2)_5OCH_3$ stabilizes a lamellar phase from 15 up to 80 wt%. Surprisingly, two separate L_α regions were observed, one at concentrations between 15 and 35 wt% and one between 60 and 80 wt%. Similar features were observed for a trisiloxane surfactant the hydrophilic part of which consists of 10 polyoxyethylene units [16,17]. Due to the lack of experimental data, the influence of the molecular structure on the formation of a disconnected L_α phase could not be discussed at that time.

In our previous study [8] we demonstrated that the highly diluted and the disconnected L_α phase are not two different phenomena but that they belong together. In this study the development of a continuous L_α phase extending to low concentrations ($C_{10}E_4$) into an L_α phase restricted to high concentrations ($C_{10}E_5$) was investigated. Surprisingly, the addition of $C_{10}E_5$ to $C_{10}E_4$ did not lead to a continuous shrinking of the L_α phase from the dilute side (thus remaining connected to the concentrated L_α phase) but first to a separation of the L_α phase before the highly diluted L_α phase finally disappeared. On the basis of phase diagrams and ^{2}HNMR measurements we claimed (a) that the disconnected L_α phase is a general feature of non-ionic surfactants, (b) that there are no structural differences between the connected and the disconnected L_α phases, (c) that the disconnection only takes place if the distance between two bilayers equals the thickness of the bilayers, and (d) that the disconnection is tuneable by the rigidity of the monolayer.

In order to provide further experimental evidence for these claims we studied the phase behavior of the pseudobinary system water–pentaethylene glycol dodecylether/hexaethylene glycol dodecyl ether ($H_2O–C_{12}E_5/C_{12}E_6$) as a function of the surfactant composition δ and the total surfactant concentration γ. Mixtures of $C_{12}E_5/C_{12}E_6$ were chosen as, according to [8], the disconnection can be tuned simply by mixing two surfactants, one of which forms a continuous L_α phase extending down to low concentrations ($C_{12}E_5$), whereas the other L_α phase is restricted to high concentrations ($C_{12}E_6$). The phase diagrams were monitored by visual observation, the type of the lyotropic liquid crystals was determined via polarization microscopy, and the structural development was followed with small angle X-ray scattering (SAXS) along specific paths through the phase diagrams.

2. Experimental

2.1. Materials

The non-ionic surfactants $C_{12}E_5$ and $C_{12}E_6$ with a purity >99% were purchased from Nikko Chemicals Co., Japan. The purity of the surfactants can be judged by monitoring the critical temperature of the binary water–C_iE_j systems. The values known from literature for the purified surfactants $C_{12}E_5$ and $C_{12}E_6$ are $T_c = 32.0\,^\circ C$ at a mass fraction of $\gamma = 0.015$ [18] and $T_c = 51.3\,^\circ C$ at $\gamma = 0.025$ [18], respectively. Because the critical points for the purchased surfactants were the same within 1–2 °C as those reported in [18], the surfactants were used without further purification. Deionized (Millipore filtered) water was used for preparing the samples.

2.2. Determination of phase diagrams

To determine the phase diagrams, desired amounts of water and surfactant were weighed in glass ampoules which were sealed immediately. To attain homogeneity, the samples were thoroughly mixed using a vortex centrifuge and placed in a transparent water bath where the temperature could be controlled to ±0.02 K. The phase boundaries were determined by changing the water bath temperature in appropriate steps, thus reaching a precision of the phase transition temperatures of ±0.05 K. From the equilibrated system the number and appearance of the phases were determined visually by inspection in scattered and transmitted light. Additionally, crossed polarizers were used to detect the birefringence in the $L_\alpha + L_3 \to L_3$ phase transition, since the L_α phase shows permanent birefringence, while the L_3 phase is birefringent only under shear. In the case of liquid crystals, polarizing microscopy and/or small-angle X-ray scattering (SAXS) were used for their identification. The composition of the binary and pseudobinary mixtures is characterized in terms of the total mass fraction of surfactant in the mixture

$$\gamma = \frac{m_{C_{12}E_5} + m_{C_{12}E_6}}{m_{H_2O} + m_{C_{12}E_5} + m_{C_{12}E_6}}, \tag{1}$$

and the mass fraction of $C_{12}E_6$ in the surfactant mixture

$$\delta = \frac{m_{C_{12}E_6}}{m_{C_{12}E_5} + m_{C_{12}E_6}}. \tag{2}$$

2.3. SAXS-measurements

SAXS measurements were performed with a SAXSess camera (Anton Paar, PANalytical) equipped with the PW3830 laboratory X-ray generator with a long-fine focus sealed glass X-ray tube ($K\alpha$ wavelength of $\lambda = 0.1542$ nm) from PANalytical, a focusing multiplayer optics, a block collimator for a slit collimation, a translucent beam stop, an image plate (IP) detector, and a temperature-controlled sample holder unit (TCS 120).