

## Formation of Condensed Phase Patterns in Adsorption Layers

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We report an adsorption kinetics study on a first order phase transition in an adsorption layer. The conditions for formation of condensed phase domains within the adsorption layer of the amphiphile N-dodecyl-hydroxy-butyric acidamide (DHBAA) dissolved in the aqueous bulk phase are presented. Growth kinetics and orientational order of the domains are analyzed. The found domains have three main growth directions and are subdivided into two sections with different azimuthal chain tilt orientation. [S0031-9007(96)00183-4]

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In recent years, sensitive optical microscopy has opened up new prospects for directly observing molecular films at the air-water interface [1,2]. These techniques led to the far-reaching discovery that in amphiphilic Langmuir monolayers coexisting phases evolve structures. In particular, in the two-phase coexistence region of a high-density condensed phase and a low-density fluid phase, condensed phase domains varying in size and shape have been found [3].

Therefore the question arises as to the morphological behavior of adsorption layers or Gibbs monolayers formed by adsorption of soluble amphiphiles at the air-water surface from aqueous solutions. The quantitative understanding of adsorption layers and the effect of the adsorption kinetics on their properties have been of continuous interest. Numerous adsorption isotherms are available which take into account the interaction between the adsorbed molecules [4]. The adsorbed material has always been considered to be uniformly distributed, thus meaning that a two-dimensional coexistence region between a condensed phase and a surrounding low-density fluid phase has been ignored. However, Frumkin's isotherm provides approaches for phase transitions for strong interactions. Furthermore, in a recent theoretical paper [5], the effect of two-dimensional molecular clustering of adsorbed molecules on homogeneous surfaces has been described as a result of the competition between the entropy which trends to disperse the molecules, and the attractive interactions between molecules which tend to cause aggregation.

A prerequisite for the evolution of morphological structures in adsorption layers is the coexistence of a condensed and a surrounding fluidlike phase within the adsorption layer which is analogous to the formation of the 2D structures of Langmuir monolayers.

Recently few papers [6,7] seem to demonstrate the coexistence of two phases in adsorption layers using fluorescence microscopy or Brewster angle microscopy experiments. In these works, however, the formation of condensed phase structures was in our opinion caused by insoluble or sparingly soluble impurities: (i) in the case of sodium dodecylsulfate adsorption by dodecanol traces,

and (ii) at sodium octanoate adsorption by the presence of hexadecanoic acid as an impurity.

In two recent papers, Hénon and Meunier [8] have shown that the Gibbs monolayers formed by oversaturated solutions of the sparingly soluble hexadecanoic acid and tetradecanoic acid evolve similar domain structures as observed by Langmuir monolayers of spread fatty acids of similar alkyl chain length.

In this Letter, we present the first study on the formation and growth kinetics of a condensed phase within the adsorption layer of the amphiphile N-dodecyl-hydroxy-butyric acidamide (DHBAA) dissolved in the aqueous bulk phase. A conspicuous inflection point in the continuous course of the surface pressure transients of aqueous DHBAA solutions can be correlated with the beginning of a main phase transition for the adsorption layer. Evolution and growth kinetics of condensed phase structures have been visualized above the inflection point of the surface pressure transients by Brewster angle microscopy, and are correlated to the results of the adsorption kinetics. We have demonstrated that the condensed phase structures of the adsorption layer have a well-developed orientational order.

The surfactant N-dodecyl-hydroxy-butyric acidamide (DHBAA) used in the experiments was synthesized by Dr. R. Wagner. DHBAA was prepared by reaction of butyrolactone with dodecylamine dissolved in dioxane at 100 °C. The substance was purified by distillation and crystallization in acetone. The chemical purity ( $\geq 99\%$ ) was checked by elemental analysis and HPLC. The distilled water was made ultrapure by a Milli-Q system.

The experimental setup consists of a Brewster angle microscope (BAM) (NFT, Göttingen) connected with a computer-interfaced film balance (Riegler & Kirstein GmbH). The surface pressure was measured by the Wilhelmy method using a small filter paper to within  $0.1 \text{ mN m}^{-1}$ . The setup is contained in a cabinet which is equipped with a temperature control and a nitrogen flushing unit for preventing contaminations. The BAM images were stored using a video system which included a video recorder, a monitor, a video printer, and a

reflectivity measurement unit. The surface pressure ( $\pi$ ) transients of the dissolved DHBAA amphiphile were recorded by the film balance. For measuring the surface pressure for a selected temperature a special calibration procedure with pure water was necessary. Afterwards the water was exchanged for the DHBAA solution at  $t = 0$ . The adsorbed molecules were then completely removed by sweeping off the surface to attain a pure water surface to be used as the initial condition ( $t = 0$ ) for the adsorption kinetics measurements. The continuous registration of the surface pressure transients allows a good time resolution of the surface pressure change. The  $\pi$ - $t$  measurements were directly coupled with the corresponding BAM signals. Using the BAM device an integral reflectivity signal and the imaging of the formation of condensed phase structures were recorded. The lateral resolution of the BAM was about  $5 \mu\text{m}$ .

For all temperatures and subphase concentrations, a rapid increase in the surface pressure is observed as the initial condition ( $t = 0$ ,  $\Gamma = 0$ ) allows a rapid adsorption at the purified surface. In this state, the adsorption layer is in a fluidlike state of low density in which the adsorbed molecules or molecular clusters can move freely.

It is well established that for uniformly distributed adsorbed material discontinuities in the adsorption kinetics do not occur [4]. As similar to the equilibrium state, a discontinuity in the adsorption kinetics should indicate a phase transition within the adsorption layer. To demonstrate such abnormal adsorption kinetics, we show the surface pressure transients for the two selected aqueous DHBAA solutions ( $1 \times 10^{-5}M$  and  $3 \times 10^{-5}M$ ) at  $T = 10^\circ\text{C}$  [Fig. 1(a)]. Above a certain bulk concentration a conspicuous inflection point in the continuous surface pressure transient can be observed, whereas at lower bulk concentrations ( $\leq 8 \times 10^{-6}M$  for  $T = 10^\circ\text{C}$ ) this discontinuity disappears and the shape of the transient has the known continuous form. The inflection point in the surface pressure transients can be clearly seen, the position of which depends essentially on the DHBAA concentration of the aqueous solution. The time required to reach the inflection point shortens with increasing bulk concentration of the amphiphile.

The appearance and position of the inflection point depends considerably on the temperature [Fig. 1(b)]. The time dependence of the adsorption of  $1.5 \times 10^{-5}M$  aqueous DHBAA solution is recorded for  $T = 5$  and  $30^\circ\text{C}$ . At  $T = 30^\circ\text{C}$  the recorded transient has a continuous course representative of adsorption kinetics of uniformly distributed adsorbed molecules. At low temperatures ( $T = 5^\circ\text{C}$ ) the pronounced inflection point in the  $\pi$ - $t$  adsorption kinetics can again be observed which indicates a phase transition in the adsorption layer. At a critical condition, corresponding to the first occurrence of the inflection point at a critical surface pressure, the adsorption layer seems to reach a critical state above which a second condensed phase similar to that observed in Lang-

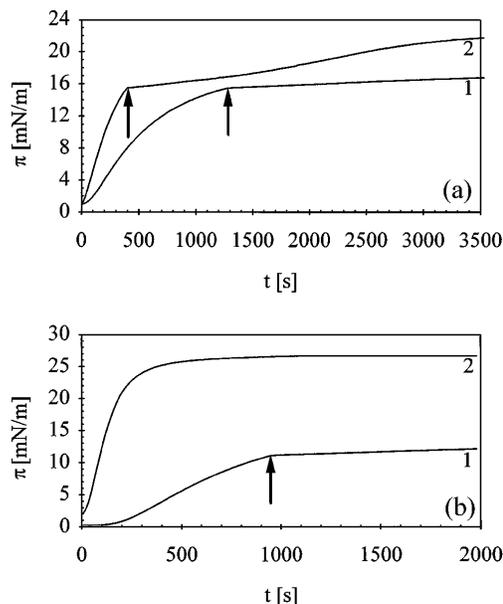


FIG. 1. The phase transition during the adsorption kinetics of DHBAA starts at the discontinuity of the  $\pi(t)$  curve. (a) The phase transition in the adsorption layer occurs above a critical concentration of the aqueous solution. The onset of the phase transition depends on the bulk concentration: (1)  $1c = 10^{-5}M$ , (2)  $c = 3 \times 10^{-5}M$  DHBAA at  $T = 10^\circ\text{C}$ . (b) The phase transition in the adsorption layer depends on temperature for a given concentration of the aqueous solution ( $1.5 \times 10^{-5}M$ ). At low temperatures [(1) for  $T = 5^\circ\text{C}$ ] the phase transition begins at about 950 sec, whereas at the high temperature [(2) for  $T = 30^\circ\text{C}$ ] no phase transition can be observed [continuous  $\pi(t)$  curve].

muir monolayers is formed. Above the critical surface pressure, the increase of the surface pressure is drastically reduced. A slight linear increase in surface pressure is recorded.

The evolution of a newly formed condensed phase of the adsorption layer on a microscopic scale can also be observed by the simultaneously recorded reflectivity signal. No phase transition is indicated if the overall  $\pi$ - $t$  adsorption kinetics have a continuous course, and under these conditions the formation of condensed phase structures can never be observed with BAM. On the other hand, a careful inspection by BAM of the transients with a conspicuous inflection point has shown convincingly that the condensed phase structures can be observed only after an induction time beyond the inflection point, i.e., the thermodynamically induced phase transition. In Fig. 2, the transients of surface pressure and reflectivity are compared. The reflectivity increases spontaneously after the induction time when the phase transition was already indicated by the inflection point in the surface pressure transient. The low reflectivity which is observed in the induction time indicates that the condensed phase nuclei are not yet grown to a size of microscopic scale. The constant reflectivity suggests that in this range the supersaturation of the parent

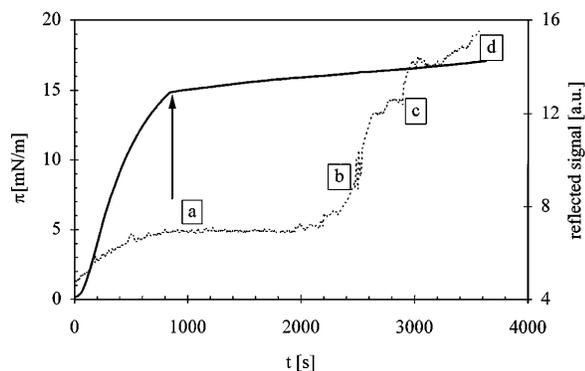


FIG. 2. Comparison of the transients of surface pressure and integrated reflectivity of  $2 \times 10^{-5} M$  DHBAA solutions at  $T = 10^\circ\text{C}$ . An induction time exists between the thermodynamically induced phase transition and the increase in integrated reflectivity where the newly formed condensed phase cannot yet be observed microscopically. BAM images of the designated points (a)–(d) were taken and are shown in Fig. 3.

phase is not high enough for the formation of nuclei of critical size. In this stage the BAM laser detects only the fluid phase of low density which contains the condensed phase nuclei of submicroscopic size. The considerably higher refractive index of condensed structures on microscopic scale provides a strong reflectivity signal. Once the size of the newly formed condensed phase structures exceeds the resolution limit of BAM (about  $5 \mu\text{m}$ ), the spontaneous increase of the reflectivity signal with time indicates a first order phase transition on a microscopic scale.

The formation of condensed phase structures within the homogeneous fluid phase of low density can be demonstrated convincingly by a sequence of BAM micrographs (Fig. 3) taken at characteristic times 3(a)–3(d) of the adsorption kinetics of Fig. 2. The images shown here are taken with a fixed orientation of the analyzer. The continuous small reflectivity without any condensed phase structures confirms that in the first growth stages the condensed phase nuclei are too small to be detected by BAM [Fig. 3(a)]. In Figs. 3(b)–3(d) the growth from microscopically small condensed phase structures to extended and branched condensed phase patterns [Fig. 3(d)] at the expense of the fluid phase is demonstrated. It is interesting to note that the growth kinetics depends largely on the appearance (occurrence) and the position of the inflection point of the  $\pi(t)$  adsorption kinetics. At a high DHBAA concentration of the aqueous solution, saturation of the fluid phase is reached after a comparably short time (Fig. 1) and the condensed phase can even cover a large part of the available monolayer area in succeeding stages of the growth kinetics [Fig. 3(d)]. The suggestion that surface-active impurities are the reason for the formation of condensed phase structures can be discounted because of the high purity and the high surface activity of the amphiphile DHBAA.

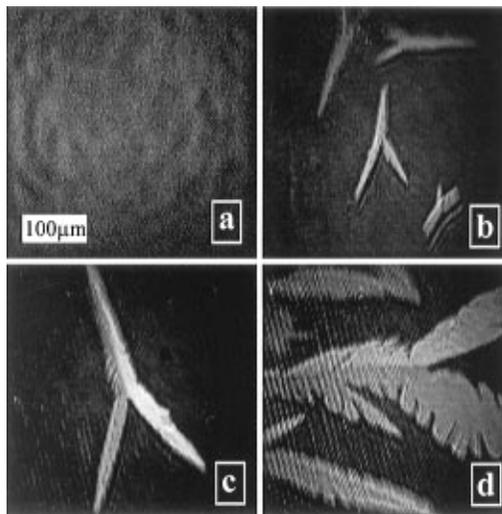


FIG. 3. Evolution of the condensed phase structures in the DHBAA adsorption layer corresponding with the designated points (a)–(d) of the transients of surface pressure and integrated reflectivity of Fig. 2 at  $T = 10^\circ\text{C}$ . (a) Condensed phase structures are in submicroscopic scale and cannot yet be seen. (b)–(d) Formation and growth of the condensed phase structures with three main growth directions within the continuous low-density fluid phase of the DHBAA adsorption layer.

The condensed phase domains formed after an induction time and at  $10^\circ\text{C}$  exhibit three growth directions. The conspicuous optical anisotropy of the domains can be seen in Figs. 3(c) and 3(d). Two growth axes form a characteristic acute intersection angle of approximately  $60^\circ$ . Each arm reflects homogeneously, but the azimuthal orientation of the two growth tips is different. The remaining most important growth axis differs basically from the other two axes and forms two obtuse angles of about  $150^\circ$  with the homogeneously reflecting growth directions. The main arm is separated by a straight line (bisector) into two sections of different uniform reflectivity. The bisector represents a defect line which separates two different azimuthal chain tilt orientations having the same orientation as the corresponding homogeneously reflecting growth tips.

All the formed condensed phase domains are contact twins. The twinned individuals show a jump of the azimuthal tilt orientation by a defined value along the main axis of the most important growth direction [Fig. 4(a)]. This can be demonstrated by analysis of the optical anisotropy. The jump of the azimuthal tilt orientation is observed if the polarizers are not crossed [Fig. 4(a)]. The twinned individuals show different brightness due to different tilt directions and the corresponding change in the polarization plane. If the analyzer is rotated, the ratio of reflected  $p$ - and  $s$ -polarized light is altered, and thus the brightness changes in dependence on the azimuthal orientational order of the growth tips. Only chain orientation parallel to the plane of incidence reflects the  $p$ -

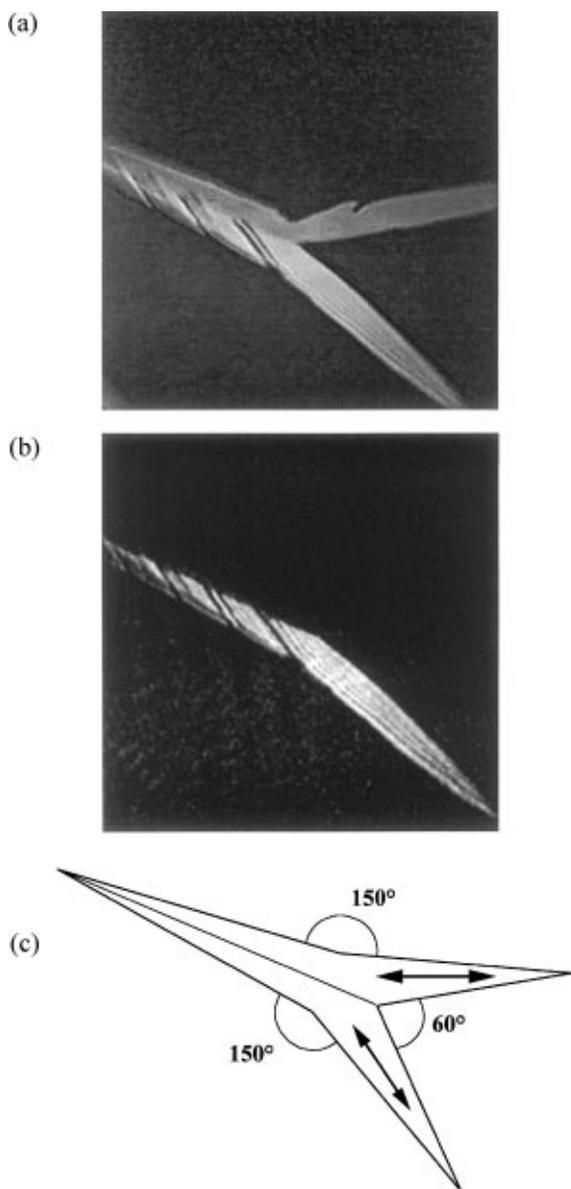


FIG. 4. Brewster angle microscopy of a condensed phase structure of the DHBAA adsorption layer at different analyzer positions: (a) polarizers neither parallel nor crossed provide high brightness for both sections, (b) one section disappears for crossed polarizers, and (c) orientational order of the molecule chains within the condensed phase structure.

polarized light without a change in polarization. In the current BAM images the plane of incidence is horizontal. Parallel polarizers give rise to largest brightness, while crossed polarizers cause lowest brightness. If the optical plane coincides with one of the homogeneously reflecting growth tips, the brightness of the corresponding domain part is drastically reduced or disappears [Fig. 4(b)] with crossed polarizers. One can show this for both homogeneously reflecting growth axes. This fact suggests that the azimuthal tilt direction of the molecules in each individual case is parallel to the homogeneously reflecting

growth axis which forms an obtuse angle of about  $150^\circ$  with the mirror line [Fig. 4(c)]. The growth direction of the segment subdivided into two sections can directly be seen because of some growth defects along the contact line of twins [Fig. 4(a)].

In summary, we have shown that in adsorption layers of amphiphiles dissolved in aqueous solution two-phase coexistence between a fluid phase of low density and a condensed phase can occur. The conditions for the first order main transition can be derived from the  $\pi(t)$  adsorption kinetics which are a function of the concentration of the aqueous solution and the temperature. The condensed phase growth patterns of microscopic size are formed first after an induction time beyond the thermodynamic phase transition. The condensed phase domains have three main growth directions and are subdivided into two sections with different azimuthal chain tilt orientation along the two homogeneously reflecting growth directions.

Synchrotron GID studies are now in progress to know the lattice structure of these adsorption layers and to relate it to the orientational order.

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