

Phase Transition in Adsorption Layers at the Air–Water Interface: Bridging to Langmuir Monolayers

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Received: October 4, 1996; In Final Form: February 20, 1997[®]

Adsorption layers of aqueous solutions of the amphiphile *N*-dodecyl- γ -hydroxybutyric acid amide are investigated using Brewster angle microscopy (BAM) and surface pressure (π) measurements. The experimental conditions for the occurrence of a first-order phase transition in adsorption layers (Gibbs monolayers) are studied. This phase transition is indicated by an inflection point in the π - t adsorption kinetics and the evolution of the condensed phase structures whose morphological features are visualized by BAM. Langmuir monolayers of this amphiphile can be obtained by the usual monolayer technique and are compared with the adsorption layers. The π - A isotherms of the Langmuir monolayers show the plateau region that corresponds to the two-phase coexistence region for the main transition between a fluid phase of low density and a condensed phase. The critical surface pressures for the main phase transitions in the adsorption layers and Langmuir monolayers are correlated. The morphological features of the condensed phase structures of the Langmuir monolayers and adsorption layers agree completely.

Introduction

Ordering processes and phase transitions in two dimensions have been of recent interest. Our understanding of the physics of Langmuir monolayers has progressed considerably because of the development of a sensitive imaging microscopy^{1–4} and its coupling with structural⁵ and thermodynamic data. An essential feature of the surface pressure (π)–area (A) isotherms of Langmuir monolayers is the pronounced plateau region that is attributed to the main phase transition between a fluid-like low-density phase and a condensed phase.⁶ It has been found that the chemical structure of the amphiphiles strongly influences the morphological properties of the condensed phases formed in the two-phase coexistence region.^{7–11}

Over several decades, a large number of papers have demonstrated the continuous interest in the adsorption and the adsorption kinetics of soluble amphiphiles at the air–water surface from aqueous solutions.^{12,13} The possibility of phase transitions in the adsorption layer has been largely ignored. Numerous adsorption isotherms are based on a uniform distribution of adsorbed molecules and thus discount the coexistence of such a low-density fluid-like phase with a condensed phase.

The question arises as to whether or not a main phase transition can occur in Gibbs monolayers that are formed by adsorption of soluble amphiphiles at the air–water interface from aqueous solutions and what the conditions are to result in a first-order phase transition in an adsorption layer. In recent Brewster angle microscopy studies, Meunier et al. demonstrated that oversaturated solutions of sparingly soluble fatty acids evolved condensed-phase domain structures similar to those observed by spread Langmuir monolayers of the same fatty acid.^{14,15} They referred also to the striking influence of surface-active impurities in soluble surfactants with respect to the formation of condensed phase domains by traces of amphiphilic impurities.¹⁶ The effect of surface-active trace components depends on the ratio of the surface activity coefficients of the main and minor components.^{17–19} Because of this high ratio in sodium dodecylsulfate (SDS), traces of long-chain alcohols

can be dominant in the adsorption layer and can evolve condensed phase domains of alcohols affected by SDS in their morphology.²⁰

To avoid such effects, the presence of highly surface-active impurities should be discounted when studying phase transitions in adsorption layers. Therefore, in the present work, we focused on highly surface-active amphiphiles soluble in water and also beyond the critical micelle concentration. In recent investigations, we found that the amphiphile *N*-dodecyl- γ -hydroxybutyric acid amide (DHBAA) is a good candidate for the investigation of a first-order phase transition in an adsorption layer. A brief report of an adsorption kinetics study with aqueous DHBAA solutions with results on the formation of condensed phase domains and, thus, a first-order phase transition in adsorption layers has been presented.²¹ In addition, the growth kinetics and orientational order of these domains were analyzed.

Recently, we developed a theoretical model that describes the adsorption kinetics of the two-dimensional, first-order phase transition in an adsorption layer. The theory includes a kinetic model of a first-order phase transition in Langmuir monolayers and adsorption layers, the adsorption from bulk solution, and the dissociation kinetics of bulk micelles.²² The prerequisite for this theoretical work was the development of an equation of state for insoluble monolayers of aggregating amphiphilic molecules that describes the main transition between the fluid-like phase of low density and the condensed phase. For aggregating numbers on the order of 10^3 and higher, the application of the first-order phase transition model is justified from a theoretical standpoint. The theoretical treatment considers the formation of two-dimensional aggregates and describes the nonhorizontal phase transition of the surface pressure (π)–area (A) isotherms as a function of the temperature.²³

The objective of the present work is to corroborate the experimental results on first-order phase transitions in DHBAA adsorption layers (Gibbs monolayers). The thermodynamic and morphological properties of the Gibbs monolayers are compared with the corresponding spread Langmuir monolayers. It is shown that a distinct inflection point that occurs in the continuous course of the $\pi(t)$ adsorption kinetics is directly related to the discontinuous transition to the nonhorizontal

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[®] Abstract published in *Advance ACS Abstracts*, April 1, 1997.

plateau region in the π - A isotherm. These characteristic features indicate the onset of the first-order phase transition. Furthermore, the morphological features of the condensed phase domains formed in the Gibbs and Langmuir monolayers are determined. The comparison of thermodynamic and morphological properties provides the experimental characteristics at which the formation and growth kinetics of the DHBA condensed phase structures occur.

Experimental Section

The amphiphile *N*-dodecyl- γ -hydroxybutyric acid amide was synthesized by reaction of butyrolactone with dodecylamine dissolved in dioxane at 100 °C. The chemical purity of $\geq 99\%$ obtained by distillation and crystallization in acetone was checked by elemental analysis and HPLC. The distilled water was made ultrapure by a Milli-Q system. The spreading solvent was chloroform p.a. (Merck).

The experimental setup consisted of a computer-interfaced film balance at which a Brewster angle microscope (BAM 1+, NFT, Göttingen) was mounted. The surface pressure was measured by the Wilhelmy method to within 0.1 mN m^{-1} using a small filter paper. The time resolution of the surface pressure measurements was $\leq 1 \text{ s}$. The light source of the BAM was a polarized 10 mW He–Ne laser, and the microscope was equipped with a polarizer and an analyzer. The reflected light is fed into a CCD camera, and the video signal is recorded on a tape. The lateral resolution of the microscope is approximately $5 \text{ }\mu\text{m}$. More details concerning BAM have been given elsewhere.⁶ The images were digitized using a frame grabber and optimized using image-processing software to enhance the contrast and to correct the distortion of the images that results from the observation at the Brewster angle. The BAM system included also a reflectivity measurement unit. Thus, an integral reflectivity signal and an image of condensed phase morphology were recorded.

Recording of the $\pi(t)$ adsorption kinetics of DHBA dissolved in the aqueous subphase was also performed with the film balance. This allows not only the direct coupling with the corresponding BAM signals but also a good time resolution of the surface pressure changes during the adsorption kinetics. Before measuring the time-dependent change of the surface pressure, calibration with pure water was necessary. Afterward the water was replaced by the DHBA solution. When the surface was swept, the adsorbed molecules were then removed from the surface to approximate the pure water surface as the initial condition ($t = 0$) for the adsorption kinetics measurements.

The π - A isotherms of this slightly soluble DHBA compound require one to minimize the time taken for the experimental procedure to minimize desorption of the spread amphiphile into the subsolution. The loss due to desorption into the subsolution decreases with an increase in the compression rate. Highly volatile chloroform was used as spreading solvent to achieve fast evaporation of the solvent ($< 1 \text{ min}$), and the π - A isotherms were recorded with high compression rates ($\Delta A / \Delta t = 0.1 \text{ nm}^2 \text{ molecule}^{-1} \text{ min}^{-1}$).

Results

The studies of a first-order phase transition in DHBA adsorption layers are based on the comparison of Gibbs monolayers formed by adsorption of the amphiphile from aqueous solution and Langmuir monolayers obtained by spreading of the same amphiphile. This allows a direct comparison between the thermodynamic behavior and the morphological features of the two types of monolayers.

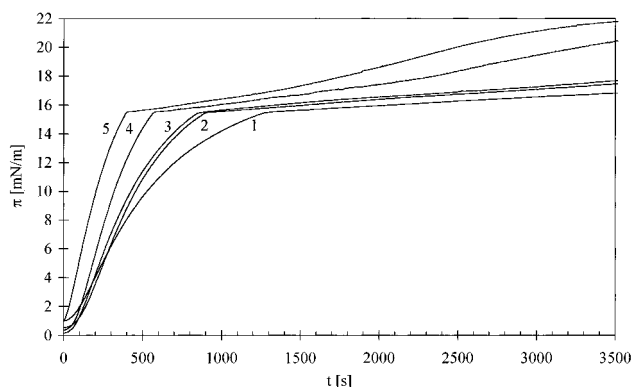


Figure 1. $\pi(t)$ adsorption kinetics of DHBA dissolved in an aqueous solution for different concentrations at $T = 10 \text{ }^\circ\text{C}$: 1– 10^{-5} , (2– 1.5×10^{-5}), (3– 2×10^{-5}), (4– 2.5×10^{-5}), and (5– 3×10^{-5} M. The inflection point in the slope of the adsorption kinetics indicates a first-order phase transition. The coordinates of the critical point (critical surface pressure π_c and the critical time t_c) for the beginning of the phase transition depends on the DHBA concentration.

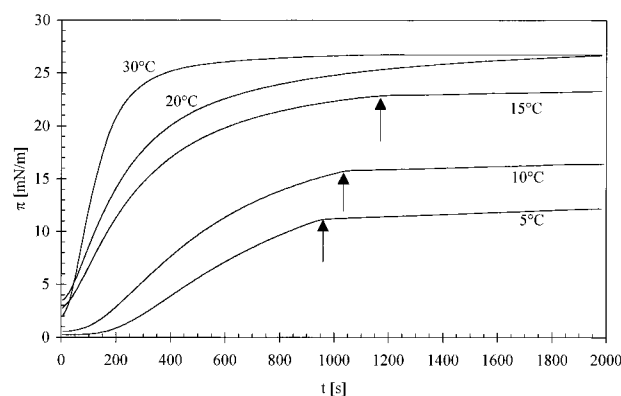


Figure 2. $\pi(t)$ adsorption kinetics of $1.5 \times 10^{-5} \text{ M}$ aqueous DHBA solution at different temperatures: 1–5, 2–10, 3–15, 4–20, and 5–30 °C. The appearance of the phase transition point and its coordinates are a function of the temperature T .

Figure 1 demonstrates the adsorption kinetics of DHBA from aqueous solution at the purified surface corresponding approximately to the initial conditions: $t = 0$, $\Gamma = 0$. It can be clearly seen that at a constant temperature ($T = 10 \text{ }^\circ\text{C}$) the $\pi(t)$ transients are affected by the DHBA concentration in the aqueous subsolution. A conspicuous inflection point exists at a critical surface pressure ($\pi \approx 16 \text{ mN m}^{-1}$ for $T = 10 \text{ }^\circ\text{C}$), which is more pronounced the higher the DHBA bulk concentration is. Beyond the inflection point, a further increase in surface pressure with time occurs but it is remarkably reduced. The corresponding critical time that is required to reach the inflection point increases the lower the bulk concentration becomes. Finally, at a certain bulk concentration ($\leq 8 \times 10^{-6} \text{ M}$ for $10 \text{ }^\circ\text{C}$), the $\pi(t)$ transient becomes continuous, as known for the adsorption kinetics of uniformly distributed adsorbed material.^{12,19} According to the results of Langmuir monolayers, such a break in the slope should indicate a phase transition within the adsorption layer.

The $\pi(t)$ adsorption kinetics is also affected by the temperature. Figure 2 shows the dynamic surface pressure curves of a $1.5 \times 10^{-5} \text{ M}$ aqueous DHBA solution for different temperatures between 5 and 30 °C. At a constant bulk concentration of the amphiphile, the appearance and position of the inflection point is determined by the temperature. For low temperatures, the transients show again an inflection point, whereas at temperatures greater than 15 °C this break in the continuity of the transients disappears. It is interesting to note that the critical surface pressure of the inflection point increases

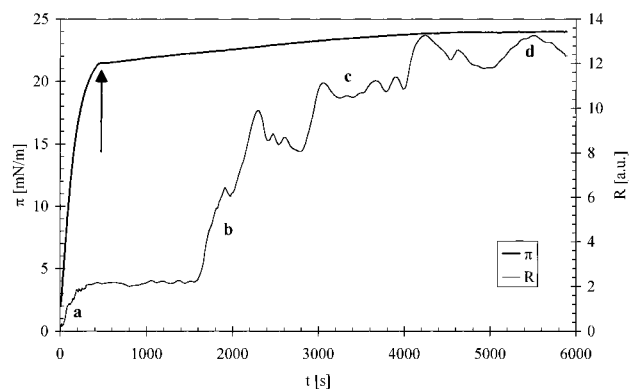


Figure 3. Transients of the surface pressure (π) and the integrated reflectivity (R) of 1.5×10^{-5} M aqueous DHBAA solution at 15°C . An induction time indicated by low reflectivity exists between the thermodynamically induced phase transition and the real evolution of the condensed phase on a microscopic scale combined with an increase in the reflectivity signal. At the designated points a–d, the BAM images shown in Figure 4 were taken.

with the temperature. The critical time required to reach the inflection point is also shifted to higher values (see Figure 2, arrows).

The simultaneous observation of the morphology of the Gibbs monolayers during the adsorption kinetics verifies that the inflection point is the critical point for the two-dimensional main phase transition.

The integral reflectivity signal obtained by BAM is a sensitive indicator for two-dimensional phase transitions, since the higher refractive index of the two-dimensional condensed phase provides a strong reflectivity signal. All the $\pi(t)$ transients that do not have a break in the slope show no significant change in the reflectivity. Under the conditions at which the inflection point appears in the $\pi(t)$ transients, a remarkable increase in the integral reflectivity indicates the macroscopic formation of a condensed phase in the adsorption layer. The transients of the surface pressure and integral reflectivity for a 1.5×10^{-5} M DHBAA solution at 15°C are presented in Figure 3. The reflectivity remains nearly unchanged over a certain time interval after the inflection point but then increases progressively. There exists thus an induction time after the thermodynamic phase transition before the new phase is sufficiently macroscopic to influence the integrated reflectivity for BAM visualization.

Evolution and growth of the condensed phase structures are in agreement with the increase in the integral reflectivity signal. Parts a–d of Figure 4 show a sequence of BAM micrographs taken at different times after the critical point of the thermodynamic phase transition. Indeed, the growth of macroscopic condensed phase structures cannot be observed before the total reflectivity increases (Figure 4a). Then the condensed phase domains reach a critical size of $\geq 5 \mu\text{m}$ and can be visualized by BAM. At temperatures of $>10^\circ\text{C}$, four main growth directions with characteristic intersection angles of 60° and 120° , but without an inner structure, are visible (parts b–d of Figure 4). The direction of the sidearms of a main axis is along the two adjacent main axes. Some steps of the growth of a single nucleus from an initial state of approximately $20 \mu\text{m}$ to a large size of more than $400 \mu\text{m}$ are shown in Figure 5. Finally, near the adsorption equilibrium, a large part of the accessible surface consists of a two-dimensional condensed phase (Figure 4d).

A different domain morphology has been observed at temperatures $\leq 10^\circ\text{C}$.²¹ The domains have here one main growth axis and two additional growth directions. The domains are subdivided into two sections with different azimuthal tilt orientation. The azimuthal tilt angle jumps by a defined angle

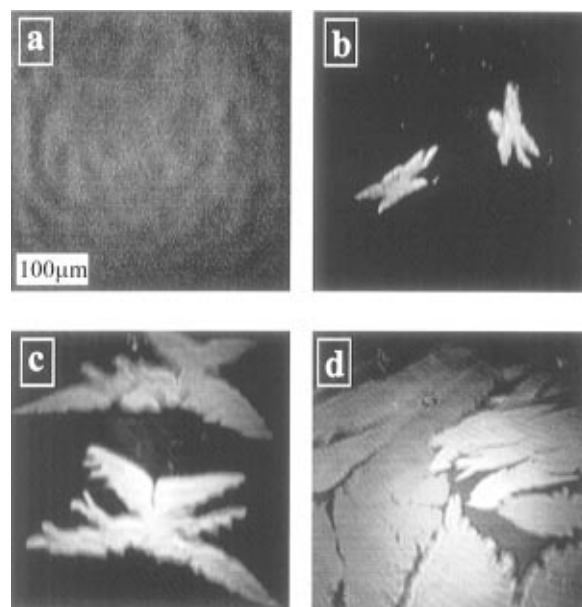


Figure 4. BAM images of the designated points a–d of the $\pi(t)$ and $R(t)$ adsorption kinetics of Figure 3. Condensed phase structures are formed in DHBAA adsorption layers at $T = 15^\circ\text{C}$. Part a shows that during the induction time the condensed phase nuclei are on a submicroscopic scale and cannot yet be seen. Parts b and c show that discrete condensed phase domains with four main growth directions grow within the continuous low-density phase of the DHBAA adsorption layer. All growth axes reflect homogeneously, indicating the same azimuthal tilt direction of the molecules. Part d shows that in a succeeding stage of the adsorption kinetics, a large part of the available surface area is covered by the condensed phase.

along a defect line of the main growth direction. The different texture types of condensed phase domains observable for $T \leq 10^\circ\text{C}$ or $T > 10^\circ\text{C}$, are shown in Figure 6. The single nuclei of the two different texture types grow to extended and branched patterns with an increasing ratio of the 2D condensed phase at the expense of the homogeneous fluid-like phase.

A comparison of these condensed phase structures formed during the adsorption kinetics of DHBAA dissolved in the aqueous bulk phase with those evolved during the compression of a Langmuir monolayer of DHBAA corroborates the striking result that in adsorption layers a condensed phase can coexist with a low-density fluid-like phase. The corresponding Langmuir monolayers were formed by direct spreading of 10^{-3} M DHBAA solution in CHCl_3 . For soluble amphiphilic monolayers such as DHBAA, the loss of monolayer material due to desorption must be considered. To minimize the material loss, the monolayer compression must be performed with high compression rates and consequently short times for the evaporation of the spreading solvent by using highly volatile solvents. The recorded π – A isotherms showed a nonhorizontal plateau region that depends on the temperature and is also a clear evidence for a main phase transition. This result corroborates the observation of a first-order main transition in the adsorption layer during the $\pi(t)$ adsorption kinetics. Recently, we have recorded π – A isotherms under different conditions and have shown that in highly compressed monolayers for compression rates of 0.007 – $0.01 \text{ nm}^2 \text{ molecule}^{-1} \text{ s}^{-1}$ mass losses due to desorption do not exceed 10%.²³ Figure 7 represents a sequence of π – A isotherms for the temperature range 3 – 25°C . Here, we introduced a linear correction factor to minimize the effect of desorption. The π – A isotherms show clearly that the critical surface pressure at which the phase transition region starts is shifted as a function of the temperature ($\Delta\pi_c/\Delta T = 1 \text{ mN m}^{-1}$

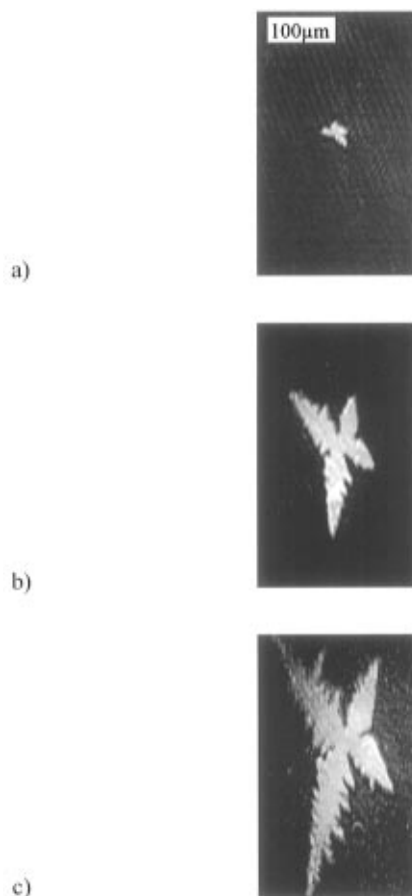


Figure 5. Selected steps of the growth kinetics of a single condensed phase domain formed during the DHBAA adsorption shown at a size of $\geq 400 \mu\text{m}$, where $T = 15^\circ\text{C}$, $c = 1.5 \cdot 10^{-4} \text{ mol/L}$, and $t_c = 1160 \text{ s}$: (a) $t = 3220 \text{ s}$; (b) $t = 3250 \text{ s}$; (c) $t = 3280 \text{ s}$.

K^{-1}). The width of the plateau region decreases with increasing temperature.

BAM micrographs of characteristic condensed phase structures formed in the two-phase coexistence region of the Langmuir monolayer are presented in Figure 8. In principle, the characteristic features of Langmuir and Gibbs monolayers agree with each other. Shape and inner structure of the domains developed at compression of Langmuir monolayers are again determined by the temperature. At temperatures of $> 10^\circ\text{C}$, the condensed phase structures have also four main growth directions, characteristic intersection angles of 60° and 120° and a homogeneous inner structure, while at temperatures of $\leq 10^\circ\text{C}$, the structures show only three growth directions and are subdivided into sections of different tilt.

Discussion

The results shown in Figures 1 and 2 indicate that the inflection point in the recorded $(\pi)t$ transients of aqueous DHBAA solutions was a function of temperature and bulk concentration of the amphiphile and occurs only under particular parameter conditions. Beyond the shown parameter values, the transients have the known continuous shape for uniformly distributed adsorbed material without a phase transition. Numerous experimental and theoretical studies demonstrate such an adsorption kinetics of amphiphiles.¹² However, experimental evidence for a phase transition in an adsorption layer at the air/water interface have not been provided until now, but the problem has been theoretically treated in some recent papers.^{24–26}

The appearance of the inflection point in the $(\pi)t$ adsorption kinetics of aqueous DHBAA solutions indicates a first-order

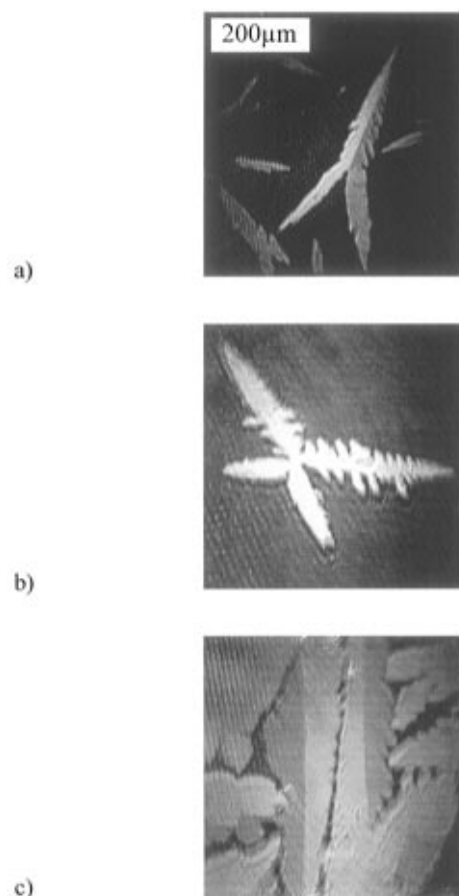


Figure 6. Morphology of the condensed phase domains of adsorbed DHBAA monolayers depends on the temperature. Part a shows that at $T = 5^\circ\text{C}$ the condensed phase domains consist of three growth directions. The main growth axis forms two obtuse angles of $\sim 150^\circ$ with the two other growth directions. The defect line of the main axis subdivides the domains into two sections that are homogeneously reflecting.²¹ The domains are contact twins at which the azimuthal orientation jumps by a defined angle along the defect line of the main growth direction. Part b shows that at $T = 15^\circ\text{C}$ the condensed phase domains exhibit four main growth directions that reflect homogeneously. Part c shows that in succeeding stages of the growth kinetics the condensed phase covers a large part of the available area. At $T = 5^\circ\text{C}$ the optical anisotropy of the textures is preserved.

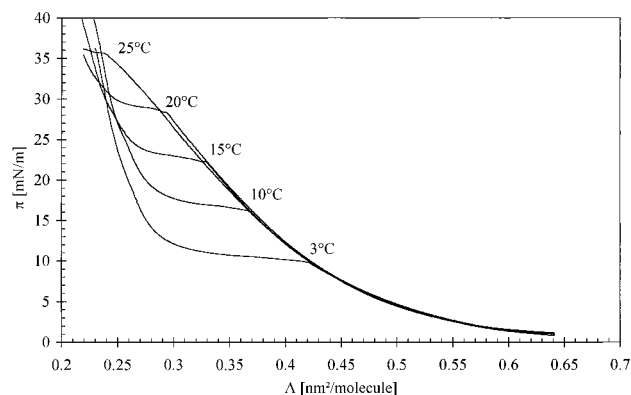


Figure 7. π – A isotherms of spread DHBAA monolayers at different temperatures.

phase transition in the adsorption kinetics. In the range from the initial conditions ($t = 0$, $\Gamma = 0$), which represents a purified surface, up to this inflection point, the rapid continuous increase in the surface pressure corresponds to adsorption in a low-density fluid-like state. The discontinuity of the $\pi(t)$ transients indicates that a condensed phase is formed that is in coexistence with the fluid-like phase. The appearance and location of the

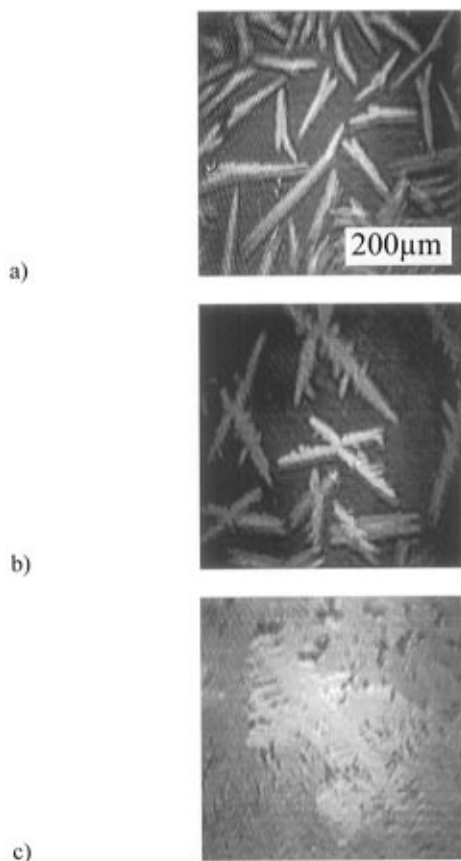


Figure 8. Morphology of the condensed phase domains that evolve at the compression of DHBA Langmuir monolayers resembles that of domains formed in adsorbed monolayers: (a) condensed phase domains formed at $T = 5\text{ }^{\circ}\text{C}$ and at $A \approx 0.3\text{ nm}^2/\text{molecule}$; (b) condensed phase domains formed at $T = 15\text{ }^{\circ}\text{C}$ and at $A \approx 0.3\text{ nm}^2/\text{molecule}$; (c) at $A \approx 0.23\text{ nm}^2/\text{molecule}$ a large part of the available area is covered by the condensed phase ($T = 15\text{ }^{\circ}\text{C}$). These domains are formed in the two-phase coexistence region behind the main transition. Their shape has the same temperature dependence as observed for adsorption layers.

critical point at which the phase transition in the adsorption layer begins depend largely on the concentration of the amphiphile in the bulk phase and the temperature (Figures 1 and 2).

The experimental $\pi(t)$ transients recorded for different temperatures show also that the critical surface pressure of the critical point increases with the temperature and is shifted to longer times. Finally, at $T > 15\text{ }^{\circ}\text{C}$ the critical point and thus the phase transition disappear. In this temperature range, only the fluid-like phase can exist.

The π - A isotherms of DHBA monolayers recorded over a large temperature region (Figure 7) demonstrate a first-order main transition and show a typical dependence of the two-phase coexistence region on the temperature. A comparison of the critical points of the main transition of the π - A isotherms with those obtained by the $\pi(t)$ transients is presented in Figure 9. The critical surface pressures of both systems nearly agree and depend linearly on the temperature. This provides conclusive evidence that the inflection point of the $\pi(t)$ adsorption kinetics corresponds to the onset of a first-order main phase transition.

According to the thermodynamic and kinetic results, the BAM images demonstrate the coexistence between a fluid-like (dark regions) and a condensed phase (bright domains) for different conditions. The morphological textures formed in the two-phase coexistence region of the $\pi(t)$ transients (Figure 6) and the π - A isotherms (Figure 8) reveal striking similarities for comparable parameters. In both systems, two different texture types of

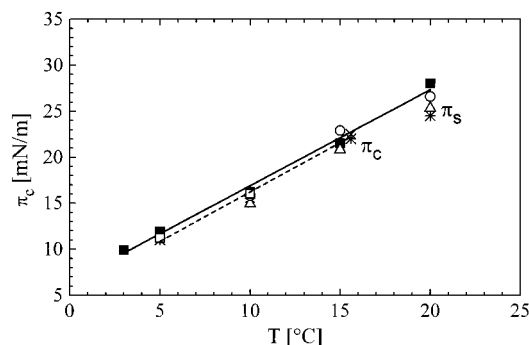


Figure 9. Comparison of the critical surface pressures of the phase transition in adsorption layers (Gibbs monolayers) and in Langmuir monolayers. For the Langmuir monolayer, the measured values ■ were fitted by linear regression (dotted line) for all temperatures. For the Gibbs monolayer, for $T < 20\text{ }^{\circ}\text{C}$ the measured values □, ○, *, △, and × obtained for different concentrations of the subsolution (1×10^{-5} to $3 \times 10^{-5}\text{ M}$) were fitted by linear regression (solid line). For $T = 20\text{ }^{\circ}\text{C}$ the surface pressure for saturation adsorption, π_s , was taken.

condensed phase domains are formed. At $T \leq 10\text{ }^{\circ}\text{C}$ three-arm domains exist that are subdivided by a defect line along the main growth axis into two sections of different uniform reflectivity. Each section has the same azimuthal tilt direction of the amphiphilic molecules. Recently, we have shown²¹ that the azimuthal tilt direction in each section is parallel to the other respective growth directions that form an obtuse angle of about 150° with the defect line. Therefore, the defect line is considered to be a mirror line of the two twinned individuals with different uniform reflectivity. At $T > 10\text{ }^{\circ}\text{C}$ the condensed phase domains develop four main growth directions and do not have any inner texture. Some steps in the growth kinetics of such a single condensed-phase structure demonstrate that shape and inner structure of the domains are preserved during the growth kinetics (Figure 5).

The principal agreement of the condensed phase textures formed in adsorption layers as well as in Langmuir monolayers is a substantial argument that highly surface-active impurities cannot be the cause for the formation of condensed-phase domains in adsorption layers. In such a case, the morphology of the domains formed by possible amphiphilic impurities of higher surface activity should be different from those evolved by the compression of the Langmuir monolayer.

The BAM studies of the two-phase coexistence region in the $\pi(t)$ transients reveal some peculiarities. For both morphological structures, a significant induction time exists between the thermodynamically determined phase transition and the real increase in the integrated reflectivity where the newly formed condensed phase cannot yet be observed microscopically. During the induction time, condensed phase structures of microscopic size do not exist and those of submicroscopic size cannot be determined. Obviously, the size of the nuclei of the newly formed condensed phase is not high enough to be detected microscopically by BAM (for the texture type formed at $T > 10\text{ }^{\circ}\text{C}$, see Figures 3 and 4). The progressive increase in the integrated reflectivity signal represents the formation of the condensed phase on microscopic scale. Actually, the single condensed-phase structures start to grow in a shape-preserving way (Figure 4a,b and 5), but at a certain size they evolve single side branches. Deviations from a continuous increase in the integrated reflectivity as can be seen in Figure 3 are mainly observed for the texture type formed at $T > 10\text{ }^{\circ}\text{C}$. With increasing temperature, convection cannot be completely avoided at the aqueous surface of the film trough, so a certain drift of the condensed phase domains along the surface occurs.

At a later stage the main growth axes become thicker and the single domains impinge. When the adsorption equilibrium is approached, the condensed phase can dominate, but the primary morphology of the single 2D crystals can no longer be observed. The ratio of the condensed phase formed in the surrounding fluid-like phase is mainly determined by the concentration of the amphiphile in the aqueous solution and the temperature. It increases during the adsorption kinetics and reaches the highest value at the adsorption equilibrium. Some BAM images (Figures 4d, 5c, and 6c) demonstrate impressively the dominant condensed phase in these adsorption layers.

Despite the agreement of the main morphological properties of the condensed phase domains that are formed during the adsorption kinetics (Figure 6) and at compression of Langmuir monolayers (Figure 8), it can be seen that in Langmuir monolayers the morphological features of the condensed phase are not as well developed as those of the corresponding Gibbs monolayers. This behavior can be attributed to the fact that in Langmuir monolayers more domains per area unit are formed because of the quite high compression rate that is used to reduce the material loss into the subsolution. Furthermore, the growth rate of the two systems is very different. In DHBAA adsorption layers the growth rate (v) of the domain tips is slow and amounts to $v \leq 1 \mu\text{m/s}$, whereas in the corresponding Langmuir monolayers it is $v \geq 10 \mu\text{m/s}$.

Conclusions

A special tailored amphiphile DHBAA, which can also be spread as a Langmuir monolayer, has turned out to be useful for studying the general conditions for the formation of a two-phase coexistence in adsorption layers. Conclusive experimental evidence has been provided demonstrating that a phase transition of first order can occur in the adsorption layers of amphiphiles dissolved in aqueous solution. During the adsorption kinetics, the phase transition is indicated thermodynamically by an inflection point in the continuous course of the $\pi(t)$ transients. Appearance and location of the phase transition point depend largely on the concentration of the amphiphile in the aqueous solution and on the temperature.

In the case of a phase transition in an adsorption layer, the formation of condensed phase patterns surrounded by the homogeneous fluid-like phase can be visualized by BAM. According to the measurements of the integral reflectivity signal, there is an induction time between the thermodynamic phase transition and the growth of condensed phase patterns on the microscopic scale. During the induction time, the size of the condensed phase nuclei newly formed is not large enough to be visualized microscopically by BAM.

Different types of morphological textures of the condensed phase can be formed depending on the temperature such as the

two types in DHBAA monolayers above and below 10 °C. Detailed information on the orientational order of the domain textures can be obtained by rotating the analyzer in the reflected laser beam.

The experimental bridging to the Langmuir monolayers supports the conclusions of a first-order main transition drawn from the adsorption kinetics studies. The phase transition point in the $\pi(t)$ transients correspond to the main transition point of the π – A isotherm. In the same temperature region, the textures formed in the two-phase region of the $\pi(t)$ transients and the plateau region of the π – A isotherms agree in the main morphological properties.

Acknowledgment. We thank Dr. R. Wagner for the preparation of the amphiphile *N*-dodecyl- γ -hydroxy-butyric acid amide. Financial assistance from the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 312, Vo 510/1-3) and the Fonds der Chemischen Industrie is gratefully acknowledged.

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