

Morphology and structural characterization of organized monolayers by Brewster angle microscopy

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Brewster angle microscopy has been involved in some of the recent advances in the field of monomolecular layers, such as the detection of a phase transition in monolayers formed by a surfactant at the solution surface, the determination of the line tension of condensed phase domains coexisting with a liquid expanded phase, as well as new insights in the role of head group interactions (e.g. hydrogen bonds) and in the organisation of biological materials in thin films.

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Abbreviations

BAM	Brewster angle microscopy
DHBAA	N-dodecyl- γ -hydroxybutyric acid amide
GID	synchrotron X-ray grazing incidence diffraction
8CB	4'-octyl-1,1'-biphenyl-4-carbonitride

Introduction

Monomolecular layers (monolayers) are formed at the air–water interface by spreading a solution of an amphiphilic molecule in an organic solvent on the surface of a trough [1]. The molecules are packed by reducing the area with a movable barrier after the evaporation of the solvent. Multicomponent monolayers are formed using mixed solutions. Adsorption of surface active molecules from the aqueous solution to the surface gives rise to a reduction in the surface tension due to the formation of the monolayer. Furthermore, binding of components, for example dye molecules, from the aqueous subphase by a monolayer of insoluble amphiphiles via electrostatic or other intermolecular interactions may result in systems in which the component is located underneath the amphiphilic monolayer. Such a bilayer system is still generally called a monolayer. These complex structures of different dyes that are being intentionally assembled are of increasing interest because they constitute truly supramolecular systems that have particular functions, such as photochemically controlled binding of target molecules from the adjacent aqueous phase. Systems of even higher complexity can be constructed by the sequential transfer of different monolayers on a solid support; these systems perform functions like molecular recognition, sensing, signal transformation, amplification and storage. The subunits (i.e. the monolayers) have to be characterized and optimized to perform their functions successfully. Brewster angle microscopy (BAM)

is a powerful technique that is perfectly suited for this purpose.

The use and quality of BAM in the optical characterization of organized monolayers has rapidly increased since its introduction in 1991 [2,3]. The physical basis of BAM is the fact that p-polarised light is not reflected from an interface between two media with different refractive indices if incident under the Brewster angle. The formation of a thin film like a monolayer having a refractive index different from those of the two media changes the optical situation, and at constant angle light is now reflected that can be used for recording and image. This method does not require the incorporation of fluorescent dyes for visualization and provides detailed information on monolayer phases, phase transitions, packing of the molecules, and chemical transformations [4]. Monolayers may be regarded as the smallest subunit of smectic liquid crystals. In analogy to those well-known systems, condensed monolayers show the same phenomena related to long-range order of molecules that implies a well-defined packing of molecules over distances that are large when compared to molecular dimensions. The characteristic textures caused by different types of long-range order are observable by BAM if the lateral size of the domains exceeds 1 or 2 μm .

Exciting new discoveries, as well as detailed investigations yielding new insights in known phenomena, that have been communicated during the period from December 1996 to December 1997, are covered in this review.

Monolayer phases

BAM has been a widely used tool for the observation and the analysis of monolayer phases [5]. Excellent examples are recent studies of the phase diagrams of fatty acid, ester, and alcohol mixtures [6•], as well as the correlation of the monolayer morphology with the results of synchrotron X-ray grazing incidence diffraction (GID) [7•].

Head group spacing and molecular tilt

Phase diagrams of surface pressure versus temperature of fatty acids have been investigated extensively using various techniques. A particular liquid crystalline phase, Ov, with long-range tilt orientational order of the long hydrocarbon chains (towards the next-nearest neighbour, NNN) was observed first using BAM [8]. The phase transitions occurring between the tilted phases L_2 (tilted towards the nearest neighbour, NN), L_2' (NNN), Ov, and the untilted phase, LS, have been investigated under isothermal conditions for mixed monolayers of octadecanoic acid and different esters of this acid, as

well as for heneicosanoic acid and two heneicosanoates in various molar ratios [6••]. The phase boundaries were marked by the rearrangements of the mosaic-like texture of the monolayer. Transitions to the LS phase were accompanied by a complete loss of contrast. With increasing molar fraction of the ester, the L_2/L_2' phase boundary moves towards lower pressure and higher temperature, whereas the L_2/O_v phase boundary moves towards lower pressure and lower temperature. The L_2' and O_v phases eventually merge and the boundary with the L_2 phase moves to zero surface pressure, in other words the L_2 phase disappears. This study has greatly improved the insight in the influence of head group lattice spacing on molecular tilt. The loss of the L_2 phase is associated with a decrease in the effective head group size which decreases the zero-pressure tilt angle.

Morphology and crystal structure in monolayers

The morphology of monolayer domains has been observed by BAM and can be related to structural data obtained by GID [9]. In more recent investigations the influence of hydrogen bonds between the polar head groups on the phase behaviour of monolayers has been analysed using amphiphilic hydroxy acid amides. In the case of N-tetradecyl- β -hydroxy-propionic acid amide the surface pressure area isotherm shows two plateau regions indicating first-order phase transitions for temperatures below 15°C. The phase transition at higher surface pressure is particularly interesting [10•]. The general lattice structure of the two phases involved is very similar, and the arrangement of the alkyl chains remains unaltered. The changes in the conformation of the head groups, however, indicate differences in the hydrogen bonding in the two phases [10•].

In a second case, monolayers of the enantiomers and of the racemic mixture of N-tetradecyl- γ,δ -dihydropentanoic acid amide have been investigated using BAM and GID [7••]. The racemate as well as both enantiomers, form stable monolayers showing the same surface pressure–area (π -A) isotherm with a temperature-dependent first-order phase transition from a liquid-expanded to a condensed phase. The shapes of the dendritic domains of the condensed phase formed upon monolayer compression, however, differ considerably. The BAM images show mirror symmetry in the domains of the *R* and *S* enantiomers and a different shape for the domains of the racemate. The two main growth axes of the enantiomers form an intersection angle of 143° at a temperature of 15°C. The directionality of the hydrogen bond interactions in the head groups determines the preferred growth directions, whereas in the racemic mixture the interaction between the enantiomers eliminates the symmetry effects and causes growth in two main directions. The GID results show that the hydrocarbon chains are tilted to NN. The positional correlation length is larger for the (11) reflex than for the (10) and (01) reflexes, and it has been proposed [7••] that the direction of formation of infinite

chains of hydrogen bonds is perpendicular to the tilt direction.

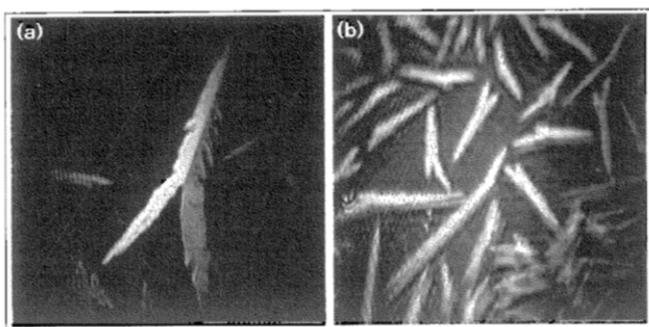
Phase transitions in adsorbed monolayers

Monolayers are formed at the surface of aqueous solutions of surfactants by adsorption and can be detected by measuring, for example, the reduction of the surface tension of the solution [11]. A general question concerning these adsorption layers (Gibbs monolayers) is whether phase transitions occur. Remarkable studies have answered this question using BAM and surface pressure measurements [12,13••]. The adsorption kinetics of the surfactant N-dodecyl- γ -hydroxybutyric acid amide (DHBA) has been measured at various concentrations of the aqueous solution and at a particular concentration for different temperatures [13••]. Discontinuities (break points) have been observed in the adsorption isotherms as well as in the temperature-dependent kinetics for temperatures below 20°C. The BAM images recorded during adsorption clearly reveal the formation of domains in a condensed phase (Figure 1a). To support the interpretation of these results of the formation of a condensed phase, monolayers of DHBA have been formed by spreading a solution in chloroform and compressing these Langmuir monolayers. Although the surfactant is partly lost in the subphase because of its limited solubility, π -A isotherms have been recorded as high compression rates. These isotherms clearly provide evidence for a first-order phase transition, and BAM images show the formation of condensed phase domains (Figure 1b) that are very similar to those observed upon formation of the Gibbs monolayer. Furthermore, the surface pressures at which the phase transition begins during adsorption and the surface pressure in the π -A isotherms for the onset of the phase transition in the Langmuir monolayers coincide and show the same temperature dependence. This investigation settles a long standing question and a theoretical model has been developed to describe the kinetics of the two-dimensional phase transition in Gibbs monolayers [14].

Monolayer flow

Depending on the monolayer phase, an induced flow may reorient domains—which occurs during the transfer from the water surface to a solid support by the Langmuir–Blodgett technique—or it may deform them. In two dimensions, an elongational flow field is expected to produce a long string-like structure. An important parameter here is the line tension of two-dimensional monolayer domains. The line tension is the energy per unit length of a border line between two monolayer phases. Therefore, a large line tension causes domains of a liquid-condensed phase surrounded by a liquid-expanded phase in a monolayer to assume a circular shape with minimized length of the border line, whereas a small line tension may lead to dendritic or elongated domain shapes. This parameter is not easily accessible, and BAM measurements have provided opportunities to determine it [15]. The relaxation of bola-shaped and

Figure 1



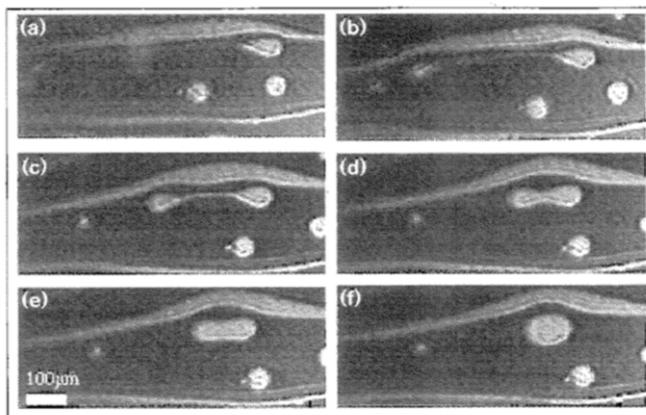
Morphology of domains of condensed phase surrounded by monolayer of liquid-expanded phase of *N*-dodecyl- γ -hydroxybutyric acid amide (DHBAA). (a) A monolayer formed by adsorption from the 1.5×10^{-5} M aqueous solution of DHBAA, temperature 5°C. (b) A monolayer formed by spreading from a 10^{-3} M solution of DHBAA in chloroform on pure water and compressing into an area $A = 0.3 \text{ nm}^2/\text{molecule}$ at 5°C. Reproduced with permission from [13**].

elongated domains after a shear distortion leads to the same value of line tension [16]. The deformation and relaxation processes of monolayer and bilayer domains have been investigated and analysed in order to determine the respective line tensions [17**]. The material used, 4'-octyl-1,1'-biphenyl-4-carbonitrile (8CB), is known to form monolayers at the air-water interface that undergo a phase transition upon compression to a bilayer phase at a surface pressure of about 5 mN/m and molecular areas between 0.40 nm^2 and 0.09 nm^2 . An extensional flow field was applied by a four-row mill. The relaxation of a bola-shaped bilayer domain is shown in the series of BAM images in Figure 2. Initially, the domain has the typical bola-shape (Figure 2a to 2c) but then assumes an elliptical shape that relaxes into a circular disc. The line tension is calculated from the relative velocity of one end of the bolas over a certain period of time (e.g. 2.5 s, depending on the properties of the monolayer). The monolayer line tension is of the order of $1.2 \times 10^{-12} \text{ N}$, whereas the line tension of the bilayer domains is much larger, $1.1 \times 10^{-11} \text{ N}$. This may be due to the fact that the bilayer consists of interdigitated 8CB molecules. The attractive dipole-dipole interactions therefore should be stronger in the bilayer than in the monolayer, leading to an increased line tension of the bilayer domains. This extremely interesting study provides new insights in the intermolecular interactions in a complex structure.

Non-equilibrium structures and hysteresis effects

During the usual measurement of surface pressure-area isotherms the surface pressure is recorded while continuously decreasing the area. It is assumed [18*] that the monolayer is in thermodynamic equilibrium, and sometimes this is verified by sequentially reducing the area by small fractions and allowing the monolayer to relax. Nevertheless, the establishment of thermodynamic

Figure 2



Relaxation of an elongated bilayer domain of 8CB having an area of $0.27 \text{ nm}^2/\text{molecule}$ after application of an extensional flow field; time of relaxation: (a) 0 s; (b) 0.67 s; (c) 1.33 s; (d) 2.0 s; (e) 2.17 s; (f) 2.5 s. In (a) to (c) the domain has a typical bola-shape consisting of two almost circular disks connected by a thin string and becomes elliptical (e) and approaches a circular shape (f). Reproduced with permission from [17**].

equilibrium in the monolayer is not trivial, in particular during compression in a nearly horizontal section of the π -A isotherm that is typical for a first order phase transition where no or very small surface pressure gradients occur in the monolayer. Upon rapid compression of a monolayer across a phase transition, non-equilibrium structures like dendritic domains of the more condensed phases are formed quite often and they relax into circular domains. The extent of branching correlates with the supersaturation, as demonstrated in the case of 1-monopalmitoyl-*rac*-glycerol monolayers [18*] by recording BAM images during the relaxation process.

Brewster angle autocorrelation spectroscopy has been used to determine the tilt angle of the hydrocarbon chains in monolayers of octadecanol and to investigate the behaviour near the triple point in the phase diagram involving the $L_2'/\text{LS}(\text{Rot I})/\text{LS}(\text{Rot II})$ phases [19*]. L_2' is a phase with tilted chains, whereas the chains are vertically oriented in the $\text{LS}(\text{Rot})$ phases. In the $\text{LS}(\text{Rot})$ phase the vertically oriented hydrocarbon chains may rotate around their axis. The phases $\text{LS}(\text{Rot I})$ and $\text{LS}(\text{Rot II})$ differ in the lateral packing. In the $\text{LS}(\text{Rot I})$ phase, the chains show orthogonal packing, whereas this is hexagonal in the $\text{LS}(\text{Rot II})$ phase. As in a previous investigation of eicosanol monolayers with BAM [20], the order of the different transitions has been investigated with the transition $L_2'/\text{LS}(\text{Rot I})$ being of first order, whereas the transition $L_2'/\text{LS}(\text{Rot I})$ is of second order. The same domain morphology as before the phase transition is found when returning to the LS phase (for example by decompression) after a short residence time (a few seconds) in the $\text{LS}(\text{Rot})$ phases. Such a memory effect was found which is particularly detectable in the vicinity of the triple point [19*].

vertically oriented hydrocarbon chains may rotate around their axis. The phases LS(Rot I) and LS(Rot II) differ in the lateral packing. In the LS(Rot I) phase, the chains show orthogonal packing, whereas this is hexagonal in the LS(Rot II) phase. As in a previous investigation of eicosanol monolayers with BAM [20], the order of the different transitions has been investigated with the transition $L_2'/LS(\text{Rot I})$ being of first order, whereas the transition $L_2'/LS(\text{Rot II})$ is of second order. The same domain morphology as before the phase transition is found when returning to the LS phase (for example by decompression) after a short residence time (a few seconds) in the LS(Rot) phases. Such a memory effect was found which is particularly detectable in the vicinity of the triple point [19*].

Pronounced hysteresis effects have been found by measuring π -A isotherm compression–expansion cycles with monolayers of poly(L-glutamic acid) at the air–water interface [21]. This material, after spreading on an acidic subphase (pH=1.5), forms helical rods that are organised side-by-side. Repeated compression–expansion of the monolayer results in the formation of a rigid layer as shown using BAM. The transformation is tentatively interpreted as being caused by a helix–coil transition and interdigitating of the polymer chains.

Changes of monolayer morphology due to relaxation processes as well as hysteresis effects like those described here have been observed and recorded by BAM. These observations clearly demonstrate that monolayers may reach the energetically most favourable molecular organization, in other words the thermodynamic equilibrium, quite slowly. Therefore, BAM is an extremely useful tool to verify the state of the monolayer.

Monolayers of new materials

Since the morphology of monolayers at the air–water interface is directly visualised and important information on the packing of the molecules in the monolayer is provided by BAM without addition of probe molecules, this technique has been used to investigate a variety of new amphiphiles. Such materials are being synthesised with the aim of assembling systems on the molecular scale with particular functions like switching, rectification, charge conduction, signal transduction and energy conversion. The monolayer behaviour of a novel class of disc-shaped amphiphiles with an edge-on orientation of the disks that is required for charge conduction in the monolayer plane has been studied using various techniques including BAM. Immediately after spreading, solid, optically anisotropic domains are formed due to strong intermolecular interactions [22].

A crown-ether C_{60} derivative has been studied in monolayers as an amphiphile that has two functionalities; the fullerene unit with a high energy of association and the crown-ether moiety that is capable of forming

complexes with monovalent ions thereby enhancing the intermolecular repulsion as well as anchoring the whole molecule to the water surface [23]. The monolayer was stabilised by the addition of KCl to the aqueous subphase and the molecular area increased close to the theoretical value by the interaction of K^+ with the crown-ether moiety. The aggregation properties are also modified in the presence of KCl as detected by BAM.

Monolayers of unsubstituted C_{60} form domains of a condensed phase with 'holes' of gas-analog phase after spreading at an area of $270 \text{ nm}^2/\text{molecule}$ and nearly 0 mN/m surface pressure [24].

New amphiphilic ferrocene derivatives have been synthesised in order to form well-defined monolayers and Langmuir–Blodgett films. The monolayer behaviour clearly demonstrates that the bulky ferrocene unit requires more than one alkyl chain combined with a hydrophilic function for the formation of stable monolayers. Derivatives with one chain only, therefore, have to be co-spread with an intercalant like octadecane to fill the space [25*].

Ultrathin films of poly(di-n-hexylsilane) have been prepared by co-spreading with arachidic acid. The spectroscopic changes of the monolayer upon compression have been interpreted by a transition from disordered poly(di-n-hexylsilane) chains to an ordered zig-zag (crystalline) conformation [26]. This transition takes place at about 25 mN/m , in other words the surface pressure of the L_2/S phase transition of the arachidic acid matrix. The BAM images show optically anisotropic domains reflecting the state of the polymer.

In an attempt to incorporate non-amphiphile supermolecules in organised monolayers a ruthenium–rhodium complex can be co-spread with an amphiphile anchor, stearic acid, due to the positive charge of the dyad. The mixed monolayers were investigated using various techniques including BAM [27*]. Surprisingly, the complex dyad remains at the air–water interface even upon compression to areas where the stearic acid matrix layer cannot accommodate all the dyad molecules underneath it. The formation of a phase with a bilayer or multilayer of dyad, therefore, has been assumed. BAM images provide evidence for this organisation of the system [27*].

An interesting photoresponsive material investigated in monolayers at the air–water interface is a poly(vinyl alcohol) derivative with azobenzene sidechains. The surface pressure–area isotherm of the *trans*-isomer differs strongly from that of the *cis*-isomer, and the reversible photochemical interconversion causes mechanical changes of the monolayer, for example an expansion at a surface pressure of 5 mN/m upon formation of the *cis*-isomer. Such photochemical effects may play an important role in reversible binding of molecules from the aqueous subphase to the monolayer. BAM images revealed clear

differences in the morphological and rheological properties between the *trans*- and *cis*-isomer formed by reversible photoisomerisation [28*].

Monolayers of particular biological interest

Recently, thin films that are formed from biological material of particular importance, like the lung surfactant or the Meibomian gland secretion, have been studied at the air–water interface. The human lung surfactant protein, SP-B, and its amino terminus, SP-B_{1–25}, strongly modify the behaviour of palmitic acid monolayers as shown by fluorescence, fluorescence polarisation, and BAM [29*]. In particular, the formation of condensed phases is inhibited. Upon continuous compression, most monolayers undergo a phase transition to 3D amorphous material at elevated surface pressures, and this phenomenon is called collapse. This process can be reversible with formation of a monolayer from the collapsed material upon expansion (respreading). The collapse process of palmitic acid monolayers is altered with increased collapse pressure and facilitated respreading of the monolayer upon expansion. This is essential for the *in vivo* function of the lung surfactant in facilitating uptake of gases in the lung. The modification of the collapse behaviour is illustrated in Figure 3 [29*]. Figure 3a shows the monolayer of palmitic acid on a buffered saline (0.15 M NaCl, pH = 6.9, 25°C) prior to collapse. Figure 3b shows the fracturing of this monolayer upon collapse. Figure 3c, a monolayer of palmitic acid with 20 weight % SP-B_{1–25}, shows nucleation and collapse of small domains.

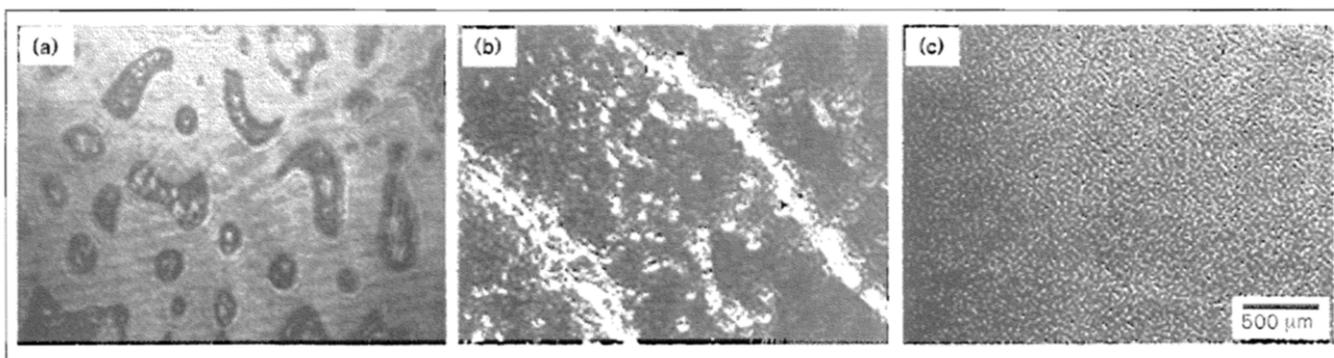
The Meibomian gland secretion forms a thin layer covering the tear film on top of the eye ball. In most of the published studies of this layer a thickness between 100 nm and 520 nm has been assumed. In a recent *in vitro* BAM investigation of such films at the air–water interface [30], optically isotropic areas of both relatively

high reflectivity and areas with smaller reflectivity were observed. With a refractive index of the thin film of 1.47 the values for the thickness of the films are 5.0 ± 0.1 nm (phase with high reflectivity) and 0.84 ± 0.02 nm (darker phase). These values seem very reasonable in the view of the biological function of the film. As a protective layer, the film should not interfere with vision and this is achieved by having a low refractive index and low reflectivity which is the retardation of water evaporation and protection from particles in the air as well as from invasion of micro-organisms. Therefore, the thin film on the Meibomian gland secretion is wiped from the surface of the tear film by each motion of the lid, typically several times per minute, and immediately reformed. Such a protective layer has to be as thin as possible (a biological membrane has a thickness typically of 5–6 nm) in order to meet with the dynamic requirements and to avoid waste of the biological material.

Conclusions

BAM has developed into a powerful tool for the characterisation of monolayer morphology, the detection of long range order in monolayers and the determination of important parameters like the polar tilt angle of hydrocarbon chains. For example, the phase transitions in adsorbed layers of surfactants at the solution surface were discovered using this technique. BAM also plays a particular role in the determination of the line tension of condensed phase domains surrounded by a liquid-expanded phase and has provided new insights in the structure and behaviour of films formed from biological materials or polyfunctional supermolecules. In the near future, these types of film, which are composed of molecules with complex structure and designed function, will gain increasing interest. BAM provides unique possibilities to enhance progress in the organisation of polyfunctional materials in supramolecular architectures.

Figure 3



Effect of the amino terminus, SP-B_{1–25}, of lung surfactant protein on the collapse behaviour of monolayers of palmitic acid on a buffered saline subphase (0.15 M NaCl, pH = 6.9, 25°C); (a) fusion of condensed phase of a pure palmitic acid monolayer upon compression prior to collapse; (b) bulk fracturing of this monolayer upon collapse; (c) collapse behaviour of a monolayer of palmitic acid with 20 weight % SP-B_{1–25}; this monolayer shows nucleation and growth of small collapsed phase domains. Reproduced with permission from [29*].

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