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Brewster angle microscopy: A preferential method for mesoscopic characterization of monolayers at the air/water interface

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ABSTRACT

Knowledge of the mesoscopic morphology of condensed phase domains formed after the main phase transition in the two-phase coexistence region of Langmuir monolayers progressed rapidly with the development of the highly-sensitive imaging techniques, particularly by Brewster angle microscopy (BAM). Latest developments of commercial BAM instruments have been developed to a high technical level and allow upgrading to imaging ellipsometers which combine optical microscopy and ellipsometry and make the assessment of small layered structures or patterned thin films possible. A large variety of condensed phase domains different in mesoscopic sizes and shapes as well as their textural features has been observed which depend sensitively on the chemical structure of the amphiphilic monolayer and the system conditions, such as surface pressure and temperature. This unsuspected morphological variety of condensed phase domains has been proven not only in Langmuir monolayers but also in adsorbed monolayers (Gibbs monolayers), in Langmuir monolayers penetrated by dissolved surfactants or in adequate molecular recognition systems. The inner textures of domains can be explained on the basis of their geometry and the two-dimensional lattice in dependence of the tilt angle of the alkyl chains and gave rise to the development of a geometric concept on the basis of the molecular packing. New knowledge has been gained about non-equilibrium structures and their transition kinetics into the equilibrium state. Combined results obtained recently by BAM have enhanced the understanding of molecular organization in phase diagrams and binary mixtures. Recent advances in model studies about chiral discrimination effects and of the highly specific structural changes of host-monolayers by recognition of non-surface active guest-components have made progress. Semi-empirical quantum chemical methods have been used to gain insight into the role of different types of interactions involved in the main characteristics of mesoscopic length scale aggregates of mimetic systems.

1. Introduction

The air/water interface represents a unique hetero-dielectric medium where two phases with completely different dielectric constants are in contact [1]. Therefore, amphiphilic monolayers at the air/water interface have been utilized as models for extensive studies of more complex systems. For the characterization of monolayer model systems it is advantageous that the interface is molecularly flat and in a dynamic state as well as the easiness with which the experimental variables can be manipulated.

Over many decades of the 20th century, surface tension measurements were the main source of information about monolayers at the air/water interface. The existence of condensed monolayer phases could be concluded from the existence of the plateau in the surface pressure–molecular area (π–A) isotherms. However, measurements of π–A isotherms provide thermodynamic results and consequently, evidence and characterization of structural phenomena at mesoscopic level are excluded when alone this technique is used.

The introduction of two highly-sensitive imaging techniques, namely the fluorescence microscopy and Brewster angle microscopy (BAM) allowed new insights into the mesoscopic morphology and ordering of condensed phase domains formed in the two-phase coexistence region of Langmuir monolayers [2,3].

The fluorescence microscopy, developed some years before BAM for the direct observation of molecular films at the air–water interface yielded first microscopic evidence for the coexistence of two phases in the plateau region of the π–A isotherm [4]. In fluorescence microscopy, an insoluble fluorescent amphiphilic marker must be added to the monolayer material which is excited using a high-pressure mercury lamp. Then, the monolayer state is observed with a microscope mounted with a camera. A variety of probes such as 4-(hexadecylamino)-7-nitrobenzoxa-1, 3-diazole, L-α-phosphatidylcholine-β-(NBD-aminohexyl)-γ-palmitoyl, *sn*-1, 2 dipalmitoyl-3-glycerophosphatidyl ethanolamine (DPPE) sulfo rhodamine, dipalmitoyl nitro benzooxadiazolphosphatidyl ethanolamine (DP-NBD-PE) and 1-palmitoyl-2-{2-[(7-nitro-2-1, 3 benzoxadiazole-4-yl) amino] dodecanoyl} phosphatidylcholine (NBD-PC) have been used. The contrast arises from the different solubility of the probe in

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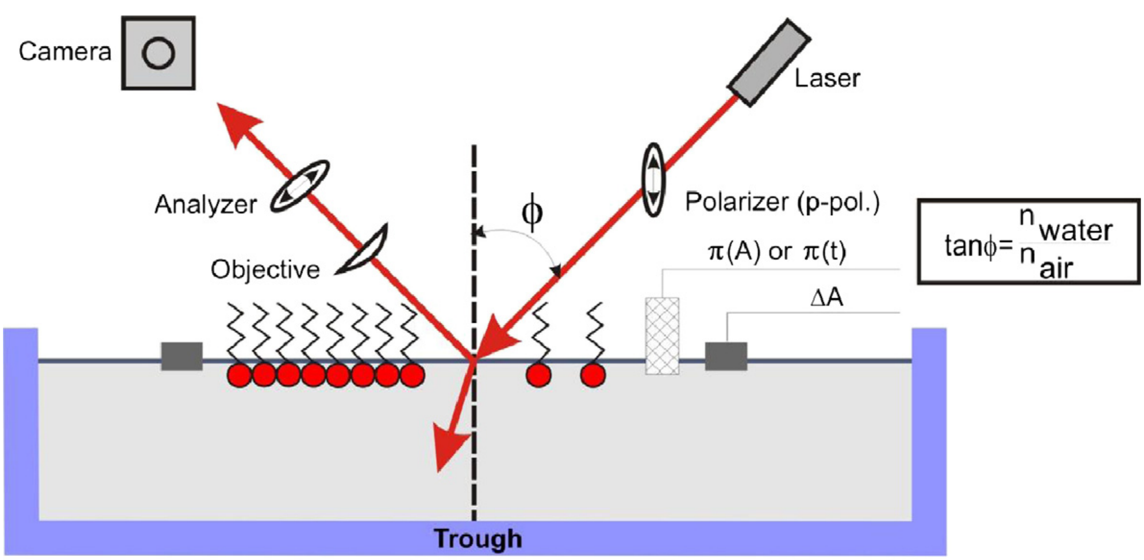
the two phases. However, the application of fluorescence microscopy has two disadvantages. Firstly, in some cases, the addition of trace components, also of fluorescent probes, to the main component of the system can considerably modify its properties. Secondly, crystalline and highly ordered phases reject the fluorescent molecules. The drawbacks of the fluorescence microscopy are discussed in detail by Meunier [5]. External probes are not necessary by the BAM technique and it is therefore advantageous compared to the fluorescence technique. Starting in 1991 [2,3], with the Brewster angle microscopy (BAM) a powerful method was developed which allows visualizing the morphology of amphiphilic monolayers on mesoscopic scale without any external perturbation. In the meantime, Brewster angle microscopy has developed to technical perfection and excellent commercial instruments are offered.

The introduction of BAM confirms the far-reaching finding that the plateau region of π–A isotherms of amphiphilic monolayers represents a two-phase coexistence region between a condensed phase of high density and a fluid phase of very low density. A large variety of condensed phase domains different in sizes and shapes has been found which depend sensitively on the chemical structure of the amphiphilic monolayer and the system conditions, such as surface pressure and temperature. An unsuspected morphological variety of condensed phase domains has been proved not only in Langmuir monolayers but also in adsorbed monolayers (Gibbs monolayers), in Langmuir monolayers penetrated by dissolved surfactants or in adequate molecular recognition systems. The inner textures of domains can be explained by consideration of their geometry and lattice in dependence of the tilt angle of the alkyl chains and can be described by a geometric concept on the basis of the molecular packing.

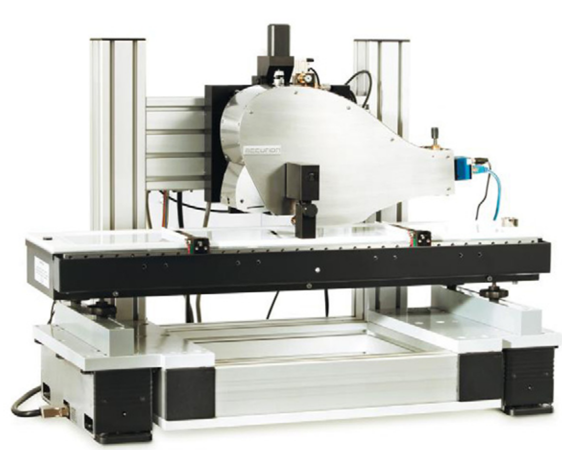
2. BAM at the air/water interface

Brewster-angle microscopy (BAM) is based on the principles of reflection spectroscopy [6–9]. At the Brewster angle of incidence, a parallel (p) polarised laser beam has zero reflectance, whereas the presence of a condensed monolayer phase leads to a change in the refractive index and thus, to a measurable change in reflectivity (Fig. 1A). Both the shape of the condensed phase domains and their inner texture can be visualized. In a typical experimental setup, a Brewster angle microscope is mounted to a computer-interfaced film balance. The microscope is equipped with a special scanning technique for providing sharp images. To obtain BAM images real in scale and angle the CCD sensor of the camera is tilted according to the Scheimpflug condition.

Since the introduction of BAM technique several commercial instruments have been available. An excellent Brewster Angle Microscope designed for the visualization of the air–water interface is the



A) Physical principle of Brewster angle microscopy.



B) Commercial instrument nanofilm_ultrabam of the Accurion GmbH [10].

Fig. 1. [10].