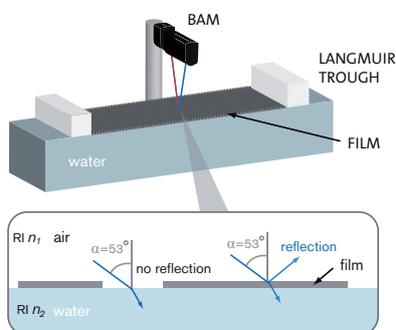


Imaging the Structure of Thin Films: Brewster Angle Microscopy

A Brewster angle microscope (BAM) enables the visualization of Langmuir monolayers and adsorbate films at the air-water interface. The images aid in understanding both the structure and flow behavior of monolayer materials.

Brewster angle microscopy

When a light beam hits a surface, it usually reflects from it. If a p-polarized light beam is directed at a clean surface at a unique angle, no reflection occurs. If the properties of the interface change, reflection will occur. This behaviour is explained by Brewster's law which describes the use of the Brewster angle (α) for a particular optical media with a refractive index of n . The principle of using the Brewster angle to obtain an image of a monolayer on water substrate is illustrated in Figure 1.



[Figure 1]: The principle of Brewster angle microscopy.

Brewster angle microscopy was first introduced in 1991 [1,2]. Since its introduction, it has become the standard technique for the imaging of thin films on liquid surfaces. When combined with a Langmuir trough, the method can be used to relate the BAM images with characteristic phase transition points in a Langmuir isotherm. This gives valuable information on the formation dynamics of the monolayer.

Key application areas

Lipid monolayers and molecular interactions. Langmuir films of lipid monolayers are often used as model structures of cell membranes. Brewster angle microscopy images at characteristic phase transitions of the surface pressure - area isotherm give valuable information on the structural and orientational changes in the monolayer. The published data includes BAM images of molecular interactions, lipids in different ionic environments and nanoparticle interactions [3-6]. Since BAM allows for direct observation of lipid monolayers during compression, it is especially valuable in the imaging of tear fluids and biological liquids [7].

Polymer and nanoparticle monolayers. The Langmuir technique has been shown to be an effective way for fabricating single-particle thick layers of lipids, polymers and nanoparticles on liquid surfaces. A Langmuir film can be transferred onto the desired substrate, creating new possibilities for fabricating nanoscale layers and functional surfaces on various materials. Recently, Brewster angle microscopy has been used for finding the optimized transfer conditions of metal nanoparticles and graphene oxide [8,9].

Petroleum industry. There is an increased interest in understanding the properties and behaviour of asphaltenes and other surface active materials in crude oil. Langmuir troughs are excellent tools for examining the layer formation of such water insoluble surfactants. In recent publications, Brewster angle microscopy has been used to show the layer formation properties of asphaltenes and model compounds [10-12].

Case study I: Imaging oleic acid in skin lipid mono-layers

Molecular interactions in membranes are of interest for example in the pharmaceutical, cosmetic and food industries. Images of the monolayer surface give valuable information on how the domain structures and film morphology change during interactions in the monolayer. The following example describes how oleic acid (OA), which is commonly used as a texture modifier in many skin care products, alters the formation and structure of model skin lipids. The full study was published in *Langmuir* 2013, 29 (15), pp 4857-4865 by Mao et al [6].

Methods

The effects of oleic acid on model skin lipids (ceramide/cholesterol/palmitic acid) and the interactions of oleic acid with different components of the lipids were examined using a KSV NIMA Langmuir trough and KSV NIMA BAM. The experiments were carried out over a wide range of surface pressure values and different lipid compositions. The phase behavior of the monolayers was monitored by examining surface pressure – area isotherms and the morphology and domain structure were visualized through Brewster angle microscopy.

Results and Discussion

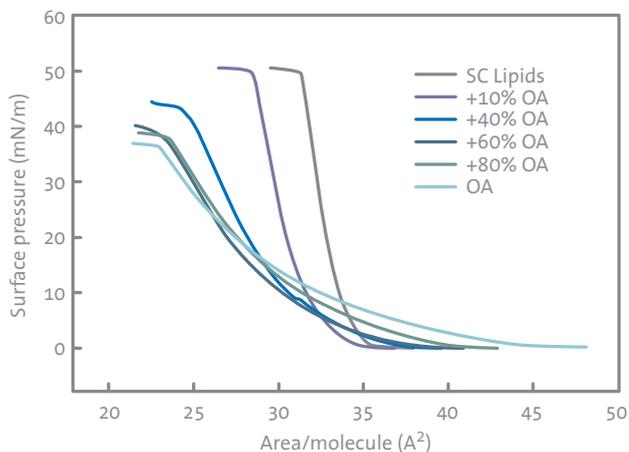
Figure 2 displays surface pressure - area isotherms for the skin lipids along with those for OA and their mixtures. Isotherms of SC lipids present a sharp increase in the surface pressure and collapse at 50 mN/m. This shows that skin lipids form rigid and condensed monolayers at the air/water interface. In comparison, the OA monolayers are much more expanded with a collapse at a surface pressure value of ~37 mN/m. With cis double bond in the middle of its acyl chain, OA cannot pack as tightly as saturated lipids and exists in a liquid-expanded phase at the air/water interface. The addition of increasing amounts of OA causes SC lipid monolayers to shift from more condensed films to liquid-expanded films and decreases the monolayer collapse pressures.

The Brewster angle images of the lipids showed that the skin lipids do not form a uniform film at the air/water interface (Figure 3A). Domains with irregular branch-like structures in bright gray are observed to be dispersed in a darker continuous domain. It is assumed that the more densely packed and more ordered palmitic acid is enriched in the bright domain and the less ordered ceramide is enriched in the darker domain.

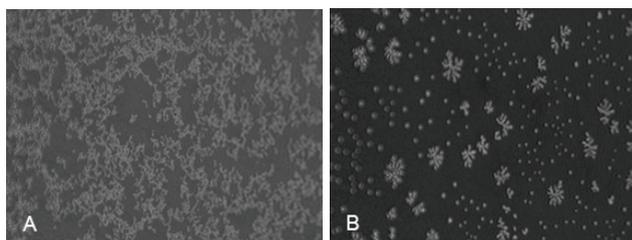
With a 40% addition of oleic acid into the skin lipids (Figure 3B), the monolayer mixture still displays phase separation into the bright domain and darker domain, but the bright domains have a snowflake-like fractal shape. The appearance of the fractal domain clearly depends upon the OA level increase from 30 to 40% and suggests that oleic acid is enriched at the fractal domains of palmitic acid.

Conclusion

Langmuir monolayer techniques were used together with Brewster angle microscopy to evaluate the thermodynamic properties and phase behavior of mixed monolayers of OA and SC lipids. The study demonstrates how the KSV NIMA BAM can be used to identify the molecular domains and follow the changes in monolayer morphology at different surface pressures for different monolayer compositions.



[Figure 2]: The isotherms of model skin lipids with increasing levels of oleic acid. With permission from *Langmuir* 2013, 29 (15), pp 4857–4865. Copyright 2013 American Chemical Society.



[Figure 3]: MODEL SKIN LIPIDS a) without and b) with 40 % addition of oleic acid at 10 mN/m imaged with KSV NIMA BAM. The size of the images is ~720 μm (W) \times 400 μm (H). With permission from *Langmuir* 2013, 29 (15), pp 4857–4865. Copyright 2013 American Chemical Society.

Case study II: Graphene oxide sheets at interfaces

Chemical exfoliation of graphite is recognized as one of the most potential methods for producing graphene in industrial scale. The result of the exfoliation process is graphene oxide, which is known to disperse well in water due to its ionizable $-\text{COOH}$ groups. However, the basal plane of graphene is essentially a network of hydrophobic benzene rings. In the following study, the properties of graphene oxide were investigated by examining the amphiphilic nature of the molecule in a Langmuir trough. The full study was published in *Journal of American Chemical Society* 2010, 132, pp 8180 - 8186 by Kim et al [8].

Methods

Synthesized graphene oxide was examined using a Langmuir trough and Brewster angle microscope from NIMA Technology. For the CO_2 flotation experiment, graphene oxide was dispersed in carbonated water. The concentration of the solution was optimized for visual observation of the floating graphene oxide sheets.

Results and Discussion

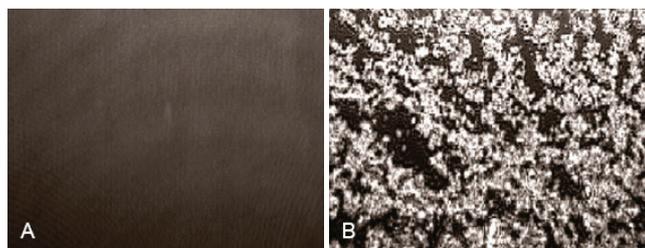
The authors examined the surface activity of graphene oxide using Brewster angle microscopy. If graphene oxide is surface active, the water surface should be covered by a layer of graphene oxide sheets. Figure 4A displays the in situ BAM image of a freshly prepared graphene oxide - water solution.

The image reveals very little surface-active material. After a few hours, graphene oxide sheets started to appear. This was attributed to slow diffusion of micrometer-sized graphene oxide sheets.

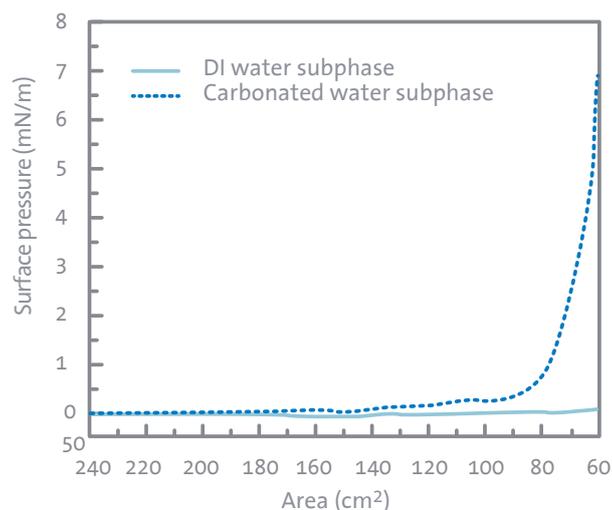
To accelerate the migration of graphene oxide to the surface, the authors designed a flotation process using carbonated water. In the process, the graphene oxide sheets adhered on to the rising CO₂ bubbles and were transported to the air-water interface. To facilitate the observation, the floating materials were concentrated by compressing the barriers in a Langmuir trough. Figure 5 presents the isotherms of graphene oxide without the flotation and graphene oxide with flotation. It can be seen that the flotation increased the surface pressure. At the same time, the Brewster angle microscopy image (Figure 4B) showed a large amount of material on the surface after the flotation process.

Conclusion

Langmuir isotherms and Brewster angle microscopy can be used to examine the properties and observe the formation of graphene oxide sheets at air-water interfaces. The study shows how monolayer imaging can be used to improve solution processing and to help finding the optimal deposition parameters for graphene oxide materials.



[Figure 4]: In Situ BAM images of a) a freshly prepared graphene oxide - water solution and b) graphene oxide with flotation. With permission from J. Am. Chem. Soc. 2010, 132(23), pp 8181-8186. Copyright 2010 American Chemical Society.



[Figure 5]: The isotherms of graphene oxide with water subphase and carbonated water subphase. With permission from J. Am. Chem. Soc. 2010, 132(23), pp 8181-8186. Copyright 2010 American Chemical Society.

Case study III: Structure of asphaltene model compounds

Asphaltenes, a class of compounds in crude oil, are known to stabilize emulsions by forming elastic interfacial films. Despite the ongoing research regarding the structure and functional groups of these polyaromatic hydrocarbons, the exact chemical composition remains unknown. In the study presented below, the interfacial activity and Langmuir film formation of model asphaltene compounds were examined using a Langmuir trough and Brewster angle microscopy. The full study was published in Langmuir 2008, 24, pp 8742-8751 by Nordgård et al [10].

Methods

Highly pure model asphaltene compounds were synthesized and dissolved in toluene or chloroform. The interfacial tension between the oil and water phases was measured using a pendant drop method. The surface pressure – area isotherms were recorded using a Langmuir trough. To visualize the film morphology, a Brewster angle microscope was used.

Results and Discussion

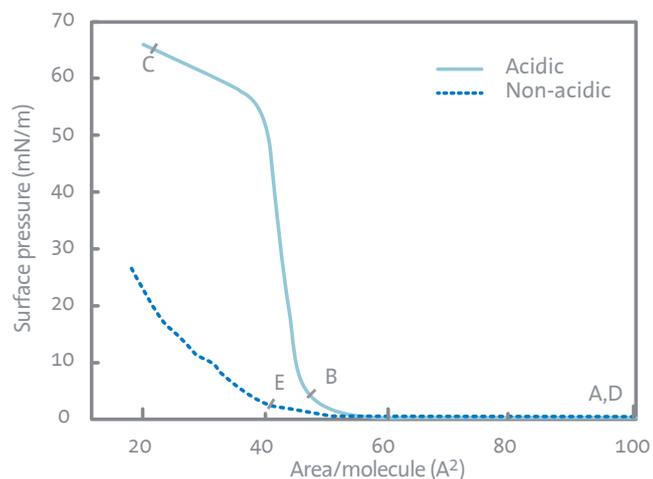
The interfacial tension measurements showed that all acidic model compounds were highly surface active while a non-acidic molecule showed only little surface activity. The Langmuir isotherms of an acidic compound and a non-acidic compound are presented in Figure 6. It can be seen that the highly surface active acidic compound was able to form a nice isotherm while the less active non-acidic molecule did not form an isotherm.

By calculating the molecular areas based on the compound structures the authors concluded that the acidic molecules were most likely arranged head-on (normal) to the water subphase surface, while the non-acidic compounds were most likely arranged flat-on (parallel) to the water subphase surface. In the head-on configuration, the molecules were able to pack efficiently and form highly organized Langmuir films. In the flat-on configuration, the non-acidic compounds were most likely arranged as stacks.

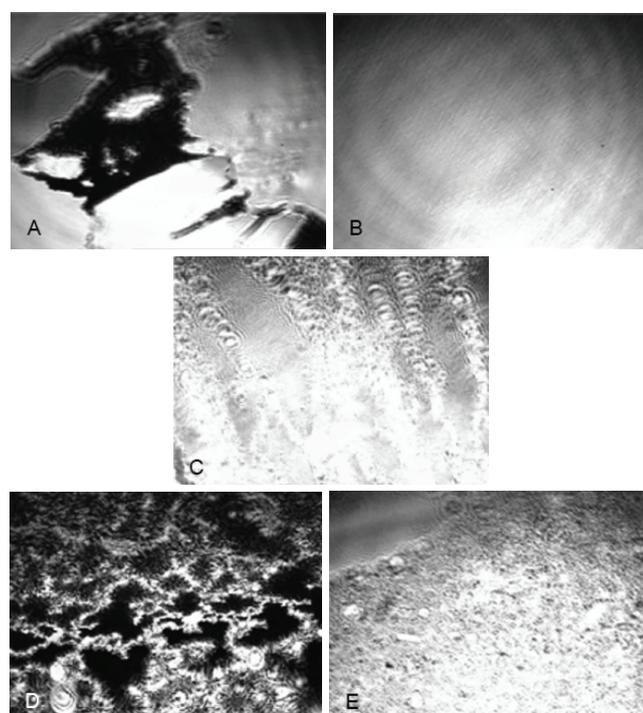
The stability of the films was further investigated using Brewster angle microscopy. Figure 7 A-C shows images taken upon compression of an acidic compound and 7 D-E of a non-acidic compound. The images correspond to the points in the isotherms marked A-E in Figure 6. In 7 A-C, a highly compressible area with condensed areas (bright) and gaseous areas (dark) is seen at low surface pressures, which turns into a smooth condensed phase when the surface pressure increases. After the collapse pressure, the film shows a “crystalline” pattern indicating multilayers. In 7 D-E, no smooth monolayer was observed.

Conclusion

Langmuir isotherm experiments show that the presence of acidic groups in asphaltene molecules is crucial for their film forming properties and interfacial activity. The packing morphology was further examined using a Brewster angle microscope. The study shows how Brewster angle microscopy can be used to correlate the structural properties and different phase transitions of Langmuir monolayers at air-water interfaces.



[Figure 6]: Langmuir isotherms of an acidic and a non-acidic asphaltene model compound. A-E explained in Figure 7. With permission from Langmuir 2008, 24(16), pp 8742-8751. Copyright 2008 American Chemical Society.



[Figure 7]: BAM images of Langmuir compression of an acidic asphaltene model compound A) before compression, B) at 4 mN/m and C) after film collapse. BAM images of a non-acidic asphaltene model compound D) before compression and E) and at 2 mN/m. With permission from Langmuir 2008, 24(16), pp 8742-8751. Copyright 2008 American Chemical Society.

Summary

Brewster angle microscopy has been shown to be a valuable method to visualize layer formation of monolayers in various application areas. KSV NIMA offers two different Brewster angle microscopes, the high-resolution KSV NIMA BAM and the compact KSV NIMA MicroBAM.

References:

- [1] Hönig, D.; Möbius, D. *J. Phys. Chem.* 1991, 95, 4590-4592
- [2] Hénon, S.; Meunier, J. *Rev. Sci. Instrum.* 1991, 62, 936-939
- [3] Ambike, A.; Rosilio, V.; Stella, B.; Lepître-Mouelhi, S.; Couvreur, P. *Langmuir* 2011, 27, 4891-4899
- [4] Korchowiec, B.; Korchowiec, J.; Hato, M.; Rogalska, E. *Biochim. Biophys. Acta.* 2011, 1808, 2466-2476
- [5] Stepniewski, M.; Pasenkiewicz-Gierula, M.; Róg, T.; Danne, R.; Orlowski, A.; Karttunen, M.; Urtti, A.; Yliperttula, M.; Vuorimaa, E.; Bunker, A. *Langmuir* 2011, 27, 7788-7798
- [6] Mao, G.; VanWyck, D.; Xiao, X.; Mack Correa, M. C.; Gunn, E.; Flach, C. R.; Mendelsohn, R.; Walters, R. M. *Langmuir* 2013, 29, 4857-4865
- [7] Rantamäki, A. H.; Javanainen, M.; Vattulainen, I.; Holopainen, J. M. *IOVS*, 2012, 53, 6442-6447
- [8] Kim, J.; Cote, L. J.; Kim, F.; Yuan, W.; Shull, K. R.; Huang, J. J. *Am. Chem. Soc.* 2010, 132, 8180-8186
- [9] Pohjalainen, E.; Pohjakallio, M.; Johans, C.; Kontturi, K.; Timonen, J. V. I.; Ikkala, O.; Ras, R. H. A.; Viitala, T.; Heino, M. T.; Seppälä, E. T. *Langmuir* 2010, 26, 13937-13943
- [10] Nordgård, E. L.; Landsem, E.; Sjöblom, J. *Langmuir* 2008, 24, 8742-8751
- [11] Álvarez, L.; Díaz, M. E.; Montes, F. J.; Galán, M. A. *Energy Fuels* 2010, 24, 1771-1780
- [12] Fan, Y.; Simon, S.; Sjöblom, J. *Langmuir* 2010, 26, 10497-10505