In-situ X-ray and neutron probe of interaction of gaseous alkanes with multilayer films

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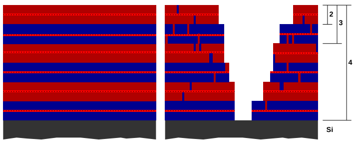
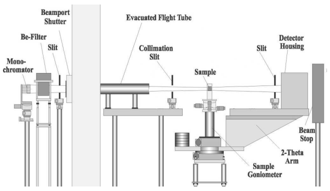
Introduction

The aim of this work was to check if the quality of Langmuir Blodgett films can be improved by exposing them to an atmosphere of organic solvents. The gas—film interactions were studied by in-situ neutron specular scattering trough a gas-flow box. Neutron scattering reveals that the increase of structural Bragg peaks is also accompanied by a decrease of super-structure peaks originated by the scattering length density difference between the sequentially stacked deuterated and non-deuterated chains. This indicates a gas assisted intermixing of amphiphilic molecules in vertical direction. This gas assisted mobility improves the quality of internal interfaces by increasing the density at the Cd-ion sites but it increases the surface roughness by the vertical pile up of molecules.

Model of a LB-multilayer:
ideal real



Experiment



The measurements were performed at the reflectometer ADAM [1] at ILL.

Test-system: 3 stacks of a per-deuterated and a non-deuterated Cd-arachidate double-layer $\mathrm{Cd}\,(\mathrm{C00\,C_{19}D_{39}})_2$ and $\mathrm{Cd}\,(\mathrm{C00\,C_{19}H_{39}})_2$.

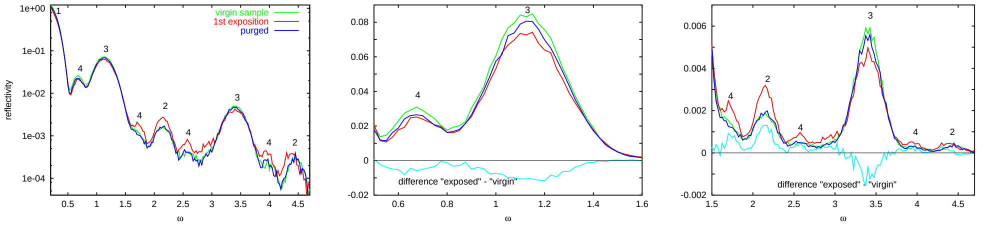
Neutron reflectivity and off-specular curves were measured:
— under solvent atmospheres reaching from 0 to saturation;
— with constant temperature (28.5° C);
— with non-deuterated solvents n-pentane . . . n-octane.

Mean scattering length densities (SLD, at $\lambda = 4.4\,\text{Å}$): $\delta_{\mathrm{CH_2}} = -1.0 \cdot 10^{-6}$,
$\delta_{\mathrm{CD_2}} = +24.9 \cdot 10^{-6}$.

Experimental results

neutron reflectivity-curves in logarithmic and linear scale of the virgin system, exposed to a saturated n-hexane atmosphere and after purging.
The numbers are expained in the table.

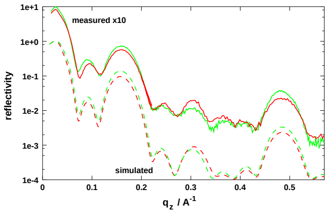
For the X-ray results see
J. Stahn et al, Langmuir Oct 2000



feature	property	peak intensity	reversibility on purging	explanation (hypothetical)
1 total reflection	scattering length density	shift to lower q	100 %	decrease of the mean SLD;
2 Bragg peak	double-layer thickness	↑ 100 %	100 %	increase of the SLD-contrast per-deuterated layer ↔ headgroups;
3 super-structure peak	2× double-layer thickness	↓ 10 %	98 %	decrease of the SLD-contrast per-deuterated ↔ non-deuterated layer; intermixing of per-deuterated and non-deuterated arachidate;
4 Kiessig fringes	multilayer thickness	↑ 50 %	100 %	shrinking of the holes?;
shift of the peaks to lower q			100 %	increase of vertical extention;
ω-scans showed no additional features				lateral correlation is not affected.

Simulation

performed with `edxr` [2]



Assumptions:

— solvent diffuses into the aliphatic sub-layers (lateral swelling of the film),

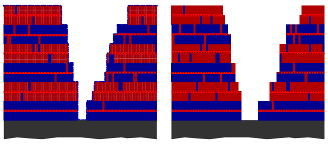
— the solvent enables a vertical exchange of arachidate,

— the swelling is completely reversible.

⇒ A qualitative agreement is achieved for Bragg- and super-structure peaks.

Filling up the holes with solvent is of no significant effect!

Model:
swollen after purging



Conclusion

The evaluation of neutron data shows that the exposure of sample to short-chain alkanes initiates a vertical exchange of fatty acid molecules which reduces the contrast of average scattering length densities between deuterated and non-deuterated layers. This behavior is similar as found at annealing [3]. In addition we indicate an increase of the peak intensities of the structural Bragg peaks for neutron scattering. This is related to an increase of the scattering contrast between the hydrocarbon chains and the head groups of molecules within the probed surface area. Both findings cannot be explained the incorporation of alkanes into the defect sites of the film because a filling of holes within the film by non-deuterated molecules does not change significantly the average scattering length density.

A larger effect can be expected assuming that the short-chain molecules enter the space between the hydrocarbon chains. The gas incorporation increases the next neighbor distances and subsequently reduces the strength of the van der Waals interaction between the amphiphilic molecules. This is accompanied by a lateral swelling of the film giving the molecules freedom to change their local position. A consequence is that the fatty acid molecules start moving across the film molecules which we observed by reduction of the super-structure peak intensities. The incorporation of short-chain molecules into organic films is not surprising. It has been observed that long-chain molecules penetrate into lipid films prepared on the water surface [4]. After exposure they remain and initiate a reduction of the aliphatic tails [5]. Also much bigger molecules, as rhodamine, were observed to penetrate trough several 100nm thick films subsequently built by sublayers of polyelectrolytes and lipids [6].

References

[1] A. Schreyer, R. Siebrecht, U. Englisch et al., Physica B 248 , 349 (1998)
[2] P. Mikulik, `edxr` — reflectivity simulation and fitting program
[3] A. Asmussen & H. Riegler, J.Chem.Phys. 104, 8151 (1996)
[4] M. Thoma, M. Schwendler, H. Baltes et al., Langmuir 12, 1722 (1996)
[5] G. Brezesinski, M. Thoma, B. Struth & H. Möhwald, J.Chem Phys. 100, 3126 (1996)
[6] U. Englisch, T.A. Barberka, U. Pietsch & U. Höhne, Thin Solid Films 266, 234 (1995)

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