Incorporation of a Non-Amphiphilic Nematic Liquid Crystal into a Host Monolayer

Valentina S. U. Fazio [a] , L. Komitov [a] , S. T. Lagerwall [a] & D. Möbius [b]

[a] MINA, Liquid Crystal Physics, Chalmers University of Technology & Göteborg University, S-41296, Göteborg, Sweden

[b] Max-Plank Institute for Biophysical Chemistry, P.O.Box 2841, D-3400, Göttingen, Germany

PLEASE SCROLL DOWN FOR ARTICLE

Incorporation of a Non-Amphiphilic Nematic Liquid Crystal into a Host Monolayer

VALENTINA S. U. FAZIO[a], L. KOMITOV[a], S. T. LAGERWALL[a] and D. MÖBIUS[b]

[a]*MINA, Liquid Crystal Physics, Chalmers University of Technology & Göteborg University, S-41296 Göteborg, Sweden and* [b]*Max-Plank Institute for Biophysical Chemistry, P.O.Box 2841, D-3400 Göttingen, Germany*

Many nematic liquid crystals are not able to form stable monolayers at the air/water interface because of the lack of a polar headgroup. A possible way to obtain a monomolecular film with these compounds is to incorporate them into host monolayers of amphiphilic compounds. Stable monolayers containing a high fraction of the liquid crystal can be obtained. We have prepared stable and transferable monolayers of MBBA (which is not an amphiphilic compound) using octadecylmalonic acid (OMA) as host. The monolayers at the air/water interface have been characterized by measurements of surface-pressure/area and surface-potential/area isotherms. The monolayers deposited on quartz plates have been characterized by determining the transfer ratio and by spectroscopic measurements.

Keywords: Langmuir-Blodgett monolayers; amphiphilic compounds; surface-pressure; surface-potential; incorporation

INTRODUCTION

Organized monolayers at the air/water interface are usually formed by spreading amphiphilic molecules, i.e. molecules that are composed of a hydrophilic head group and a hydrophobic tail [1-5]. Such monolayers can be transferred sequentially to solid substrates for the construction of designed functional assemblies [5] or to prepare multilayer systems (Langmuir-Blodgett films). The lack of a hydrophilic head group normally disqualifies a molecule for the formation of organized monolayers at the air/water interface. However, in some cases such molecules as quinthiophene have been incorporated in a matrix monolayer of am-

phiphilic molecules [6]. Another possible way to obtain monomolecular films of hydrophobic non-amphiphilic compounds is to incorporate them into host monolayers providing appropriate cavities [7-9].

The nematic liquid crystal MBBA (*N*-(4-methoxybenzylidene)-4-butylaniline) is not amphiphilic and no ordered layers of very well defined thickness of this compound can be deposited using the Langmuir-Blodgett (LB) technique. Nevertheless, we have been able to prepare stable two-component monolayers with a high fraction of MBBA incorporating it into host monolayers of the bifurcated amphiphile octadecylmalonic acid (OMA). These two-component monolayers have been transferred onto solid substrates and the organization of the MBBA molecules in the monolayers has been investigated by absorption spectroscopy.

EXPERIMENT

Monolayers at the air/water interface were prepared with a KSV3000 Langmuir-Blodgett trough held in a cleanroom environment. Ultrapure Milli-Q water (ph 5.5) was used. The molecular arrangement of the monolayers at the air/water interface has been studied by measuring the surface-pressure/area (Wilhelmy method) and surface-potential/area (vibrating capacitor method) isotherms.

LB monolayers were deposited onto quartz glass plates. The transfer ratio, i.e. the ratio of monolayer area removed from the water and solid area coated, was monitored during the deposition and the LB films were characterized by measuring absorption spectra with a spectrophotometer.

RESULTS AND DISCUSSION

Monolayers at the air/water interface

In Figure 1 the surface-pressure/area (π/A) isotherm of OMA is compared with the well known isotherm of stearic acid (C18). The two isotherms are quite different. In the case of C18 the packing of the molecules, and thus shape of the isotherm, is mainly due to the interactions between the hydrocarbon chains. Two liquid-condensed phases (LC and LC') which differ in the orientation of the chains, and a more condensed phase, also called solid phase (S) in which the carboxylic chains are vertically oriented, can be identified [1,2]. Collapse takes place at a surface-pressure of 50 mN/m. On the other hands, in the case of OMA, as pointed out by V. Vogel *et al.* [7,8], because of the
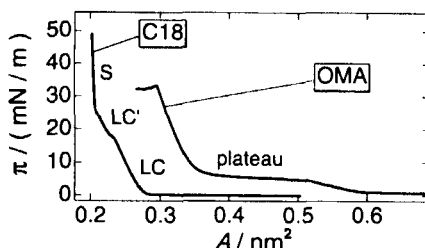
Figure 1: Comparison between the surface-pressure/area (π/A) isotherms of C18 and OMA.

presence of two carboxylic acid groups in the same molecule, the shape of the isotherm is determined by the polar headgroups. The isotherm shows a plateau between 0.51 and 0.38 nm²/molecule. Collapse takes place at a surface-pressure of 33 mN/m.

MBBA is a non-amphiphilic compound and thus cannot form stable monolayers at the air/water interface (the surface-pressure/area isotherm of pure MBBA is shown in Figure 2(a)). We prepared mixed solutions of OMA and MBBA with different molar fractions of MBBA and studied the behavior of the mixed monolayers at the air/water interface. The surface-pressure/area-per-host-molecule (π/A_h) and surface-potential/area-per-host-molecule ($\Delta V/A_h$) isotherms for the mixtures are shown in Figure 2(a), where the area-per-host-molecule, A_h, is defined as:

$$A_h = \frac{\text{area of the trough}}{\text{number of host molecules}}.$$

The addition of MBBA to the OMA matrix influences considerably OMA's π/A isotherm. On increasing the molar fraction of MBBA the plateau shrinks, the collapse pressure increases, and the shape of the isotherm resembles more and more that of a fatty acid. Moreover, all isotherms in Figure 2(a) are stable, which means that the surface-pressure is maintained with time at all areas. For molar fractions of MBBA larger than 0.5 MBBA molecules in excess are squeezed out of the monolayer during compression and the isotherms are destabilized.

To distinguish between additive and cooperative incorporation of MBBA in OMA we have plotted the collapse pressures π_c, and the areas-per-host-molecule A_h at different surface pressures, versus the molar fraction of MBBA in Figure 2(b). If the incorporation is ad-
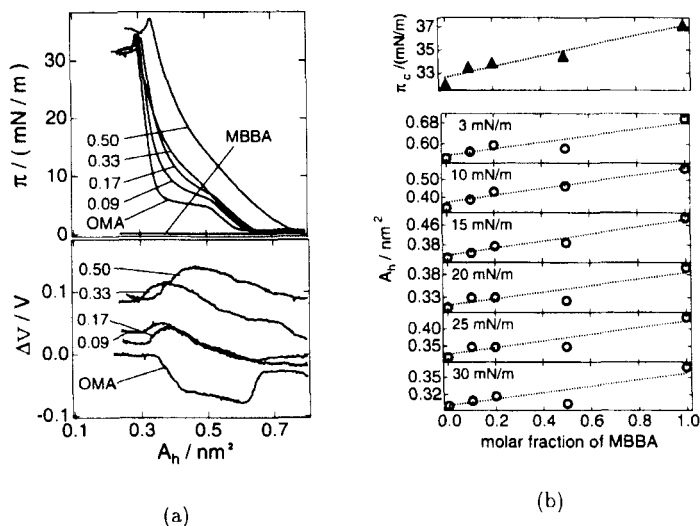
(a)

(b)

Figure 2: (a) Surface-pressure/area-per-host-molecule (π/A_h) and surface-potential/area-per-host-molecule $(\Delta V/A_h)$ isotherms for different molar fractions of MBBA, and for pure OMA and pure MBBA. (b) Dependence of the collapse pressure and the area-per-host-molecule on the molar fraction of MBBA.

ditive π_c and A_h of mixed OMA/MBBA monolayers should follow a linear relation with the molar fraction of one of the two substances [1,9]. Any deviation from this behavior would be an evidence of co-operative incorporation. In our case, as we can see from the figures, π_c and A_h follow an almost linear relation with the molar fraction of MBBA which indicates that the incorporation is additive: MBBA molecules penetrate into the chain region of the OMA monolayer as depicted in Figure 3.

The presence of MBBA also influences the $\Delta V/A_h$ isotherms. In general [1,2,7,8] the surface potential is proportional to the change of the normal component of the dipole density with respect to the pure water. For OMA ΔV is expected to be negative because this molecule has two polar heads $(\mu_{COOH} = -0.201\ D)$ and one terminal CH_3 group $(\mu_{CH_3} = +0.351\ D)$. With the addition of MBBA only the
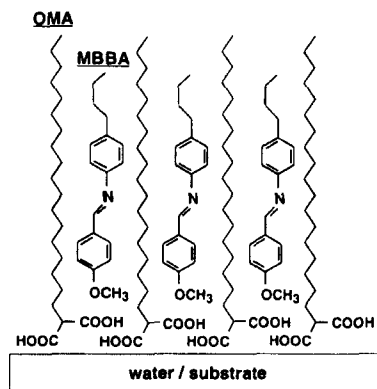
Figure 3: Scheme of MBBA molecules incorporated into an OMA matrix.

number of CH_3 groups increases and, as a consequence, the surface potential also increases and becomes positive.

The dipole moment of a CH_3 group at the interface with air has the same sign as at the interface with water. Thus, the $\Delta V/A_h$ isotherms do not tell us about the orientation of MBBA molecules in the OMA matrix. Here we assume that MBBA molecules orient as in Figure 3 since the COH_3 groups are more hydrophilic than the CH_3 ones and thus it is reasonable to think that they prefer to orient toward the polar headgroups of the host molecules [9].

Deposition

We have deposited monolayers of pure OMA and of the OMA:MBBA 1:1 mixture onto quartz glass plates.

OMA can be deposited at all surface pressures with unitary transfer ratio, provided that the deposition speed is not too large (not more than 5-6 mm/min). On the other hands, OMA:MBBA 1:1 monolayers resulted more difficult to be deposited without molecular rearrangement or collapse during the transfer onto the substrates. Deposition pressure, deposition speed, and substrate characteristics (we have also performed depositions onto ITO coated glass plates that are not reported here) can influence the transfer ratio as shown in Table 1. Good transfer ratios were obtained on quartz when depositing the mixed OMA:MBBA 1:1 monolayers at 10 and 15 mN/m at all deposition speeds.

Table 1: Transfer ratios of the OMA:MBBA 1:1 monolayers on quartz for different deposition pressures and deposition speeds. For a prefect deposition the transfer ratio should be 1.

deposition pressure	deposition speed	transfer ratio
$10\,mN/m$	$10\,mm/min$	1
$10\,mN/m$	$5\,mm/min$	1
$15\,mN/m$	$10\,mm/min$	1
$15\,mN/m$	$5\,mm/min$	1
$20\,mN/m$	$10\,mm/min$	$\ll 1$
$20\,mN/m$	$5\,mm/min$	$\ll 1$
$20\,mN/m$	$2\,mm/min$	$\ll 1$

However, transfer ratio measurements are not sufficient for the characterization of the films. We recorded UV spectra of the monolayers with the setup depicted in Figure 4. The spectra are shown in Figure 5(b) for mixed 1:1 monolayers deposited at two different surface pressures and at the deposition speed of 10 mm/min (first and third rows in Table 1).

At normal incidence ($\alpha = 0°$ in Figure 4) only a very small fraction of the light is absorbed by the mixed LB film and the spectra are almost flat. At 45 degrees angle of incidence instead, and for the same monolayers, the spectra present a structure and a peak at 326 nm. This tells us not only that MBBA is present in the LB film, but also that it is homeotropically aligned. Indeed, at normal incidence the polarization of the light lies in the plane of the glass plate perpendicular to the long axis of the MBBA molecules, and light is not absorbed. At any other incidence angle the polarization of the light has a component along the long molecular axes which is absorbed.

The fact that the films deposited at the higher surface-pressure absorb more can be explained in terms of molecular density. In films deposited at 15 mN/m surface-pressure the molecules are more densely packed and the number of MBBA molecules per unit area is about 1.6 times that of films deposited at 10 mN/m. The first films are thus expected to show absorption spectra about 60% more intense. This explains, in the limits of the experimental error [10], the differences in the spectra of Figure 5(b).
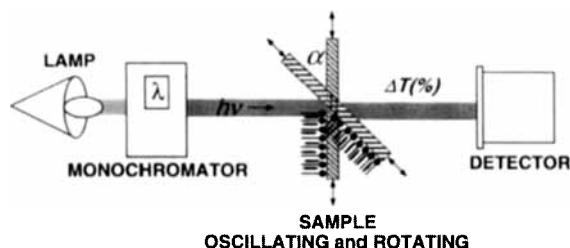
Figure 4: Setup for measuring absorption spectra of LB monolayers. The light coming from a UV-lamp is first sent through a monochromator and and then to the sample. The sample oscillates so that the light beam hits alternatively the clean part of the glass plate and the part coated with the LB monolayer. The difference in light transmission between the two cases (ΔT) is collected by a detector. The sample can also be rotated to perform the analysis at different incidence angles α.

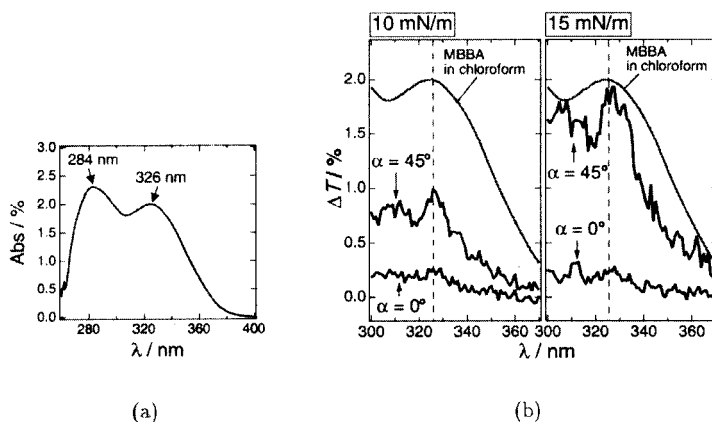(a)   (b)

Figure 5: (a) Absorption spectrum of MBBA in chloroform (0.13 mM). The spectrum presents two peaks, at 284 nm and at 326 nm. (b) Spectra of OMA:MBBA 1:1 LB monolayers on quartz glass plates deposited at two different surface-pressures. α is the angle of incidence of the light as depicted in Figure 4. At normal incidence ($\alpha = 0°$) there is almost no absorption, while a structure is present for $\alpha = 45°$.

CONCLUSIONS

We have deposited Langmuir-Blodgett monolayers of the non-amphi-
philic nematic liquid crystal MBBA incorporating it into a host mono-
layer of octadecylmalonic acid (OMA). By studying the molecular
arrangement at the air/water interface MBBA resulted to be ad-
ditively incorporated into the host monolayer. Mixed monolayers
OMA:MBBA 1:1 could be deposited at certain surface-pressures and
deposition speeds without molecular rearrangement and/or collapse.

ACKNOWLEDGMENTS

References

[1] G. L. Gaines. *Insoluble monolayers at the liquid-gas interface.* Interscience Publishers
      (1966).
[2] M. C. Petty. *Langmuir-Blodgett films: an introduction.* Cambridge University Press
      (1996).
[3] H. Bücher, K. H. Drexhage, M. Fleck, H. Kuhn, D. Möbius, F. P. Schfer, J. Sonder-
      mann, W. Sperling, P. Tillmann, and J. Wiegard, *Mol. Crys.,* **2,** pp. 199–230 (1967).
[4] H. Kuhn, D. Möbius, and H. Bücher, *Spectroscopy of monolayer assemblies.* John
      Wiley & Sons, New York (1972). Vol. 1 Part 3B pp. 577–702.
[5] H. Kuhn and D. Möbius. *Investigations of surfaces and interfaces.* John Wiley & Sons,
      New York (1993). Vol. IX B pp. 375–542.
[6] U. Schoeler, K. H. Tews. and H. Kuhn. *J. Chem. Phys.,* **61**(15), pp. 5009–5016 (1974).
[7] V. Vogel and D. Möbius. *Thin Solid Films,* **159,** pp. 73–81 (1988).
[8] V. Vogel and D. Möbius. *J. Colloid Interface Sci.,* **126**(2), pp. 408–420 (1988).
[9] W. Codroch and D. Möbius. *Thin Solid Films,* **210/211,** pp. 135–137 (1992).
[10] The experimental error is here mainly due to the fact that we compare two LB films
      that result from two different depositions.