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FLUORESCENCE PROBES IN LC-MULTILAYERS AT THE AIR-WATER INTERFACE

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Abstract The ferroelectric liquid crystal molecule HOBACPC formes multilayers at the air-water interface. Measurements of the surface contact potential exhibit an orientation of those molecules adjacent to the liquid phase. Their polar head groups point towards the water. In contrast the molecules in the second and further layers are statistically oriented. The aminostilbazolium dye di5ASPBS serves as a probe molecule which is sensitive to the surrounding dielectric constant. We have inseted the dye in a HOBACPC matrix to examine the change of fluorescence during multilayer formation on the water surface. The fluorescence exhibits some characteristic features as a function of decreasing area: a strong decrease of the amplitude shortly before the formation of the first layer and several maxima at the following layer formations. The measurement at an area above 23 $Å^2$/molecule is not reproducible due to domains larger than the measurement spot.

INTRODUCTION

Molecular layers at the air-water interface are of increasing importance in physical[1] as well as in biological[2] research. The most common model system to investigate these thin films are monolayers of surfactant molecules. A monomolecular film can form different phases at the air-water interface, depending on the surface pressure (e.g. twodimensional gas, liquid, crystal, etc.)[3]. But at high surface pressure a monomolecular film collapses to an 'undefined' state. Up to now, just a few systems forming multilayers at the air-water interface have been found[4-10] and defined.

One of the most intensively studied[11,12] substance with this interesting behaviour is HOBACPC[13]. Figure 1 shows its chemical structure. In the bulk state HOBACPC is

a thermotropic ferroelectric liquid crystal.

In case of a multilayer at the air-water interface the layer adjacent to the liquid phase is oriented with the chiral head group towards the water. The following (second, third...) layers are statistically oriented, like in a LC smectic C phase[14]. Figure 2 shows a model of the layer-growth. At different typical spots of the isotherm a sketch of the molecular arrangement (marked with capitals) is given. The HOBACPC molecule is represented by a light grey rectangular, its chiral

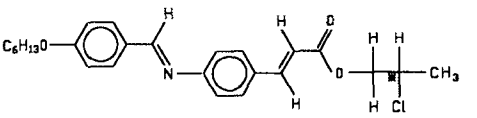

FIGURE 1 HOBACPC

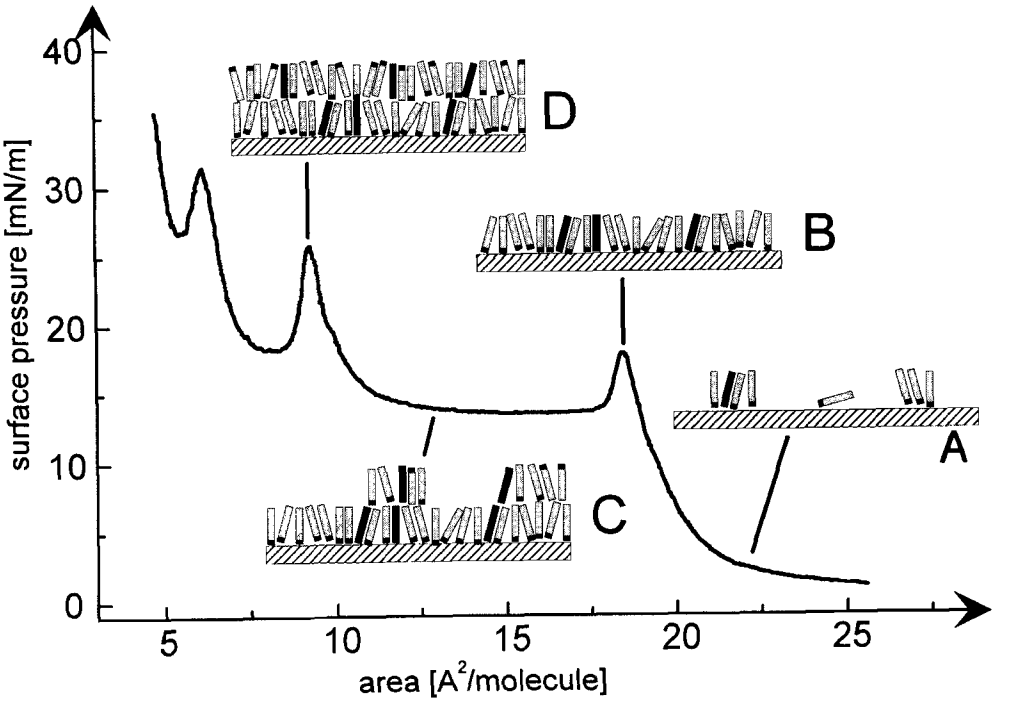

FIGURE 2 concept of a HOBACPC layer-growth

head group by a black stripe. The dark gray rectangulars symbolize dye molecules which are mixed in the LC matrix.

At position A, the area per molecule is larger then at the first collapse peak (B), a domain structure is suggested. This is assumed due to strong fluctuations of physical properties measured on a small spot, e.g. flourescence, whereas properties measured

averaged over a large surface area, e.g. contact potential difference (CPD) by displacement currence, exhibit a steady course. Here, the molecules are arranged with their head group towards the water.

On further compression, at position B, a tightly packed monolayer has been formed. The surface pressure increases until at a maximum the monolayer collapses and molecules are pushed up to form a second layer above the first one (position C).

A second collapse peak (position D) is observed at an area of exacly half the magnitude of area at the first peak. Here two complete molecular layers have been formed. This process repeats for each additional layer.

The HOBACPC matrix is doped by the aminostilbazolium dye di5ASPBS. It's chemical structure is plotted in Figure 3. The dye belongs to a class of voltage sensitive probes which are used to observe potential changes in neurons[15]. The very similar dye di4ASPBS, only differing by the length of the hydrophob alkyl endings (four instead of five carbon atoms each) has been introduced by Grinvald et al.[16] and has been studied intensively by Fromherz et al.[17]. In his paper a strong dependence of the quantum yield from the dielectric constant of the solvent is reported. In Figure 4 the quantum yield is plotted against the dielectric constant of the solvent for several solvents. Other factors influencing the quantum yield are polarity and the viscosity of the solvent.

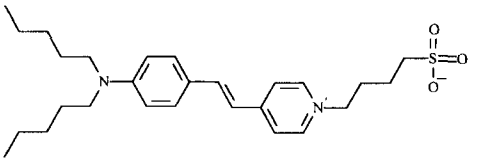

FIGURE 3 di5ASPBS

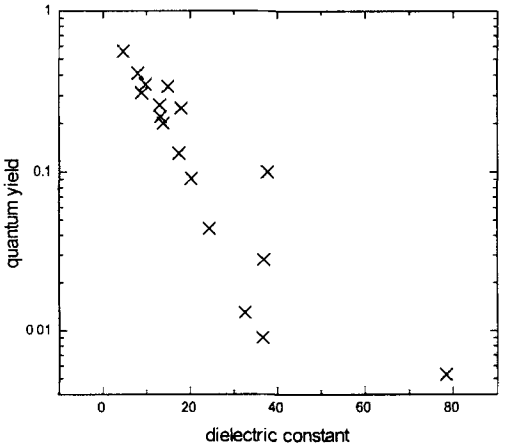

FIGURE 4 quantum yield of di4ASPBS in different solvents, from [17])

EXPERIMENTAL

Materials

HOBACPC is a gift from S. T. Lagerwall. di5ASPBS was placed at our disposal by P. Fromherz. Spreading solutions were prepared in a 5mmol chloroform (Merck, p. a.) solution. The water of the subphase was purified by a Millipore Milli-Q plus system.

Surface Isotherms

Surface pressure experiments were carried out on a Riegler & Kirstein PTFE langmuir trough. The trough was controlled by a personal computer. The barrier speed was reduced linear with the available surface. So a constant surface compression rate of 17.7%/min could be achieved. The advantages of this new compression method are a meaningfull quantification of the compression speed and a reduction of the dynamical part of the surface pressure at small surfaces. This is very important for our systems, because large compression ratios like 1:6 are often applied.

The temperature of the trough was constant 293K. Temperature dependent measurements and thermodynamical examinations of the HOBACPC system have been reported elsewhere[11].

Fluorescence spectra of monolayers

The spectral measurement of excitation and emission of molecules at the air water interface based on a commercial Spex Fluorolog 212 spectrometer. The excitation path consists of a 450W Xe lamp and a Spex 1680 0.22m double monochromator. A front-face sample geometry is applied with a mirror reflecting the horizontal beam towards the water surface and back into the emission path. The angle between the surface and the optical axis is approximately 70°. The fluorescence light is analysed by the same kind of monochromator as the excitation light and detected by a cooled photomultiplier. The whole assembly achieves a spectral resolution of 3nm. The absolute quantum yield could not be determined.

The probe was prepared by spriting a defined amount of substance in a water filled Petri dish. The subphase was always completely sucked off and refilled with a constant volume of fresh water. So the water level could be kept constant for different measurements.

For the final evaluation of the fluorescence spectra a ground substraction with

a measurement of a plain water surface was carried out.

Fluorescence change during compression

Figure 5 sketches a special apparatus, that has been developed in order to track the change of fluorescence in a monolayer during a compression experiment.

In order to measure changes in fluorescence in real time during a compression

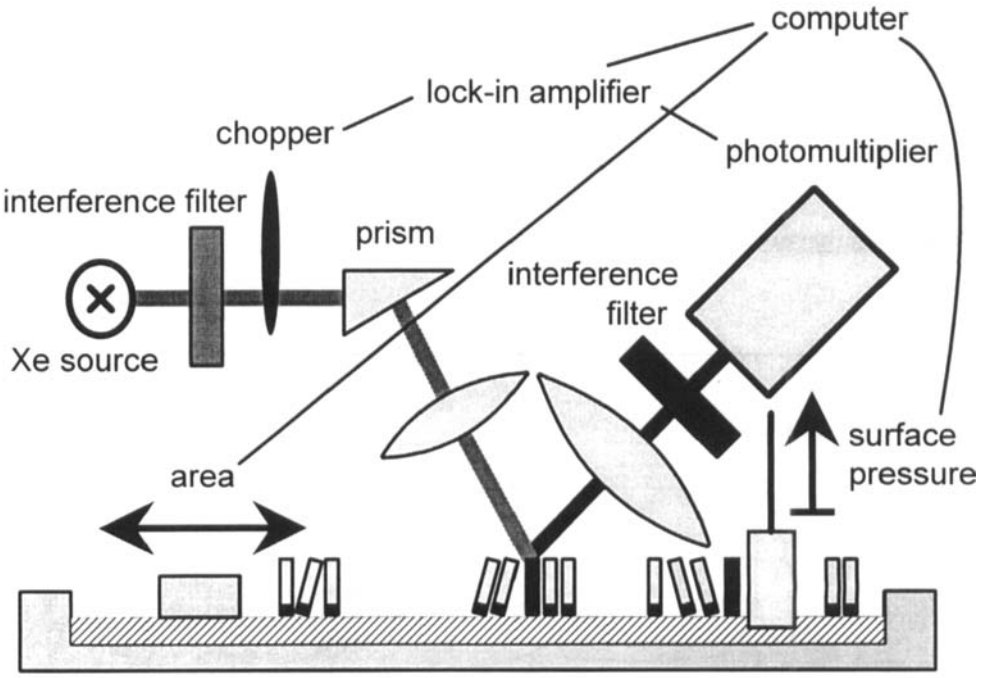

FIGURE 5 langmuir trough with fluorescence measurement

experiment, not a whole fluorescence spectrum is recorded, only one excitation and one emission wavelength are applied. This enables us also to use a lock-in amplification to increase the signal to noise ratio.

The molecular layer is sprited on a self made PTFE trough with a PTFE barrier, which is compressing with a constant speed. The data of surface pressure, available area and the result from the fluorescence measurement are stored in a personal computer.

The excitation path, on the left side of Figure 5 consists of a 100W Xe-source,

an interference filter with a halfwidth of 10nm and a transmission maximum at 497nm. A chopper modulates the light for the lock-in application and a prism deflects the light to the surface. The angle between the incident light and the surface is 60°, the angle between the surface and optical axis of the detector 45° and the angle between excitation and emission path is 90°. A neutral density filter is placed beneath the water surface to suppress the PTFE fluorescence. The fluorescence light passes a second interference filter of a transmission maximum at 607nm and a halfwidth of 10nm, before it is detected in a photomultiplier. The signal is then processed in a lock-in amplifier.

RESULTS

Mixture Isotherms

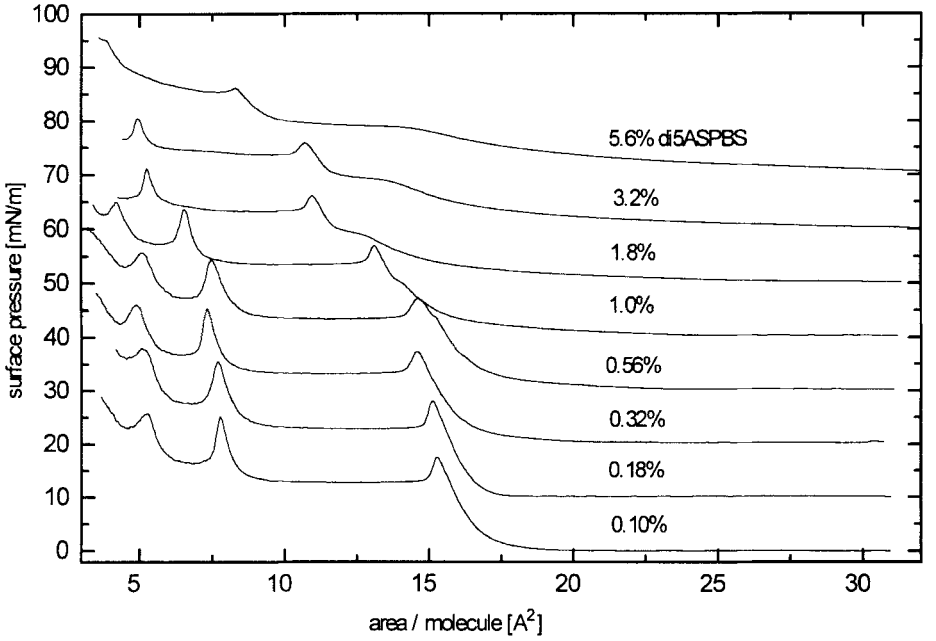

FIGURE 6 sequence of HOBACPC / di5ASPBS mixture

A sequence of mixtures of HOBACPC and di5ASPBS with a portion of di5ASPBS between 0.1mol% and 5.6mol% has been prepared. The π-A isotherms of

these mixtures have been measured and are reproduced in Figure 6.
The main aspect of these isotherms is, that the typical layergrowth of HOBACPC is not influenced by the dye addition. This is expressed by the appearance of the multiple collapse peaks.

The dye molecules are dissolved in the HOBACPC layers at low concentrations ($\leq$0.5mol%), since the π-A isotherms have practically the same appearance. But the physical state of the mixture at high concentations (>0.5mol%) must be altered since the π-A isotherms exhibit a dye concentration dependence. Our interpretation is a phase separation. This conclusion is supported by domain structure (fluorescence microscopy) in this concentration region.

Therefore the further investigation were made at low dye concentrations were made at low dye concentrations mainly at 0.5mol%.

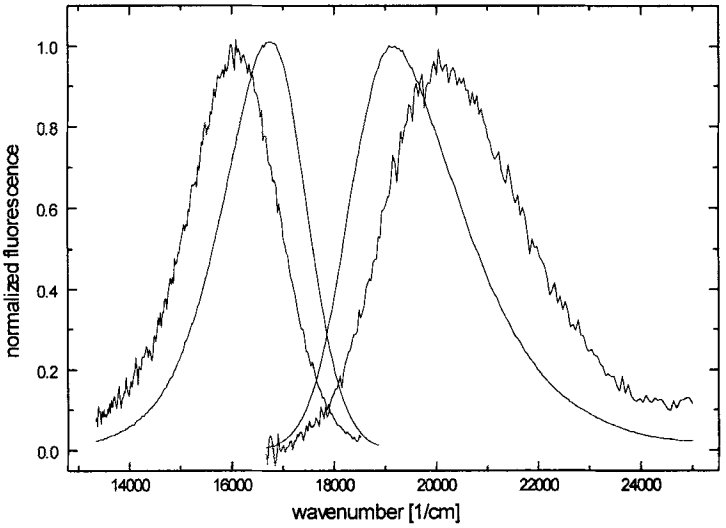

FIGURE 7 Excitation and emission spectra of di5ASPBS

Fluorescence spectra of Langmuir layers

The rough curves in Figure 7 show the excitation and emission of a 0.5% di5ASPBS in HOBACPC monolayer with 20Å per molecule area on the water surface. The maximum of the excitation curve is at 20300cm^{-1} (492nm), the maximum of the emission curve is at 16200cm^{-1} (619nm). In contrast, the smooth curves are the fluorescence spectra of a di5ASPBS in chloroform solution. Signifcant differences are

the strong blue shift of excitation for the monolayer, compared to the chloroform and analog the strong red shift of the emission.

Fluorescence change along the isotherm

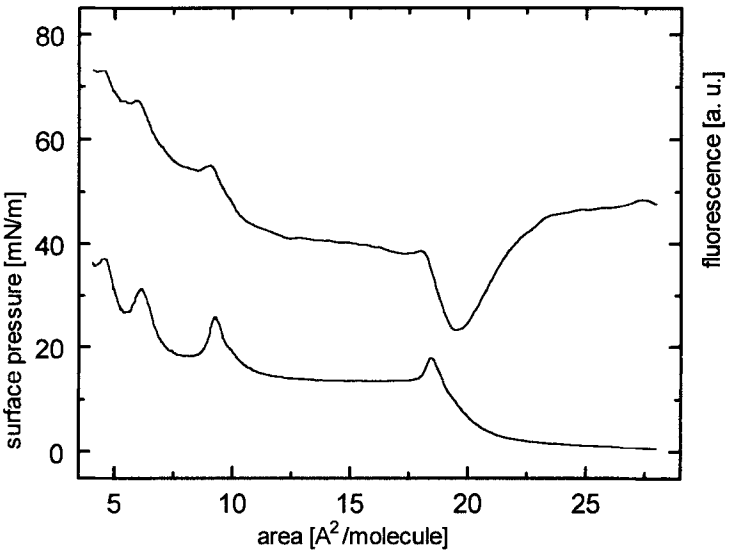

FIGURE 8 Fluorescence change during compression

Measurement of the fluorescence change during compression has been carried out with excitation wavelength of 497nm and an emission wavelength of 607nm. The chosen wavelength are close to the fluorescence maxima, as can be seen in Figure 7. Other wavelengths have also been applied, but are not further discussed here due to a small signal/noise ratio.

The fluorescence curve in Figure 8 is an averaged curve of three measurements. The single measurements don't differ from each other for areas up to 23Å²/molecule. Above this value the measurement is not reproducible due to domain structure.
At an area of 20Å²/molecule a dramatic decrease in fluorescence to about half the original magnitude could be observed. On further compression, the fluorescence intensity rises to reach a maximum at the first collapse peak. Then the intensity increases slowly during the growth of the second layer just until the second collapse peak is reached. Here, the fluorescence curve exhibits a similar behaviour as the π-A

isotherms: a local maximum at the area of the second collapse peak. This analogy repeats for all further collapse peaks.

CONCLUSION

This work has presented the possibility to dope a HOBACPC system at the air-water interface with up to 0.5mol% of the dye di5ASPBS without influencing its physical behaviour. This was proved by investigating π-A isotherms of binary mixtures between HOBACPC and di5ASPBS.

Excitation and emission spectra of di5ASPBS in a HOBACPC matrix at the air-water interface have been measured. The excitation spectrum undergoes a blue shift compared to the spectrum measured in chloroform, the emission spectrum undergoes a red shift. The position of the maxima of the fluorescence spectra are used to select the wavelengths of the fluorescence change experiment.

This experiment showed a strong correlation between the π-A isotherm and the change of fluorescence for compression experiments.

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REFERENCES

1. M. Lundquist, Prog. Chem. Fats other Lipids, Vol. 16 (Pergamon Press, 1978), p. 101.
2. M. C. Phillips and D. Chapman, Biochim. Biophys. Acta, 163, 301 (1968).
3. A. W. Adamson, Physical Chemistry of Surfaces, (J.Wiley and Sons, New York, 1982).
4. P. Erkwall, R. Erkholm and A. Norman, Acta Chem. Scand, 11, 693 (1957).

5. M. Lundquist, Proceedings of the Fourth Scand. Symp. on Surface Chemistry (Työsland, 1970), p. 70.
6. M. Lundquist, Chem. Scr., 1, 5 (1971).
7. M. Lundquist, Chem. Scr., 1, 197 (1971).
8. H. Diep-Quang and K. Ueberreiter, Polymer Journal, 13, 623 (1981).
9. B. R. Malcolm, Thin Solid Films, 134, 201 (1985).
10. C. McFate, D. Ward and J. Olmsted III, Langmuir, 9, 1036 (1993).
11. B. Rapp and H. Gruler, Phys. Rev. A, 42, 2215 (1990).
12. B. Rapp, M. Eberhardt and H. Gruler, Macromol. Chem., Macromol. Symp., 46, 134 (1992).
13. P. Keller, S. Juge, L. Liebert, L. Strezelecki, C. R. Acad. Sc. C, 282, 639 (1976).
14. M. Eberhardt, M. Geiger and H. Gruler, manuscript in preparation.
15. P. Fromherz and C. O. Müller, Biochim. Biophys. Acta, 1150, 111 (1993).
16. A. Grinvald, R. Hildesheim, I. C. Farber and L. Anglister, Biophys. J., 39, 301 (1982).
17. H. Ephardt and P. Fromherz, J. Phys. Chem., 93, 7717 (1989).