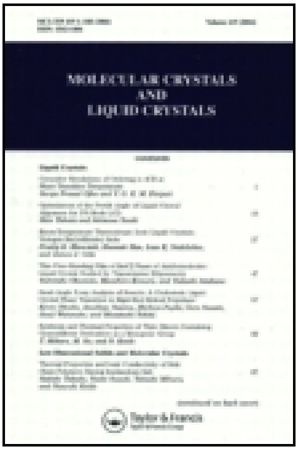

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Second Harmonic Studies of Liquid Crystal Langmuir Films

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SECOND HARMONIC STUDIES OF LIQUID CRYSTAL LANGMUIR FILMS

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Abstract The formation of pure and mixed monolayers of 4-n-octyl-4'-cyanobiphenyl (8CB) and stearic acid at the air-water interface is investigated by a combination of surface balance measurements and polarization sensitive, optical second harmonic spectroscopy. These measurements allow one to identify four different regimes upon compression of the monolayer. These regimes are an isotropic monolayer, a polar oriented phase, a compacting of the polar oriented phase, and the formation of a centrosymmetric structure. From a fit of the polarization dependence of the second harmonic intensity, the orientation of the optically nonlinear 8CB chromophores is deduced. A comparison of monolayers of different mixing ratios of 8CB and stearic acid shows, that the orientation of the 8CB molecules depends only on the surface pressure and not on their concentration in the film.

Keywords: liquid crystals, cyanobiphenyl, monolayers, second harmonic, Langmuir film

INTRODUCTION

In recent years the investigation of the physical, especially optical properties of Langmuir and Langmuir-Blodgett films has become increasingly important. These molecular films are for example intended for the use in molecular electronics, optoelectronics, as sensors or in corrosion control and as lubricants. In addition they are often used as model systems in biology, chemistry and physics [1]. Therefore, both the potential technical applications and the scientific value of these molecular films demand for a better understanding of their structure and formation process.

We have used simultaneous surface balance and second harmonic generation (SHG) measurements to study the formation of pure and mixed films of the optical nonlinear molecule, 4-n-octyl-4'-cyanobiphenyl (8CB), and stearic acid in different mixing ratios at the air-water interface during compression. Due to its restriction to noncentrosymmetric structures, the optical second harmonic generation proves to be a powerful technique for selectively probing the orientation of molecules at surfaces and interfaces. A detailed description of the SHG technique for surface analysis has been published previously in [2, 3, 4]. Surface pressure measurements provide informations about the global behaviour of the monolayer, and allow one to determine the adhesion forces of the surfactants to the water surface and their change due to the interaction of the molecules in the film. Very recently similar experiments on mixed films of 8CB and pentadecanoic acid have been performed independently by Barmentlo et al. [5].

SURFACE PRESSURE MEASUREMENTS

The Langmuir monolayers were prepared by spreading a 0.6 mM solution of surfactant molecules dissolved in chloroform on ultrapure water (Millipore Alpha-Q). In order to prevent contamination of the water surface, the trough was installed under a laminar airflow hood. After the solvent was allowed to evaporate for thirty minutes, the monolayers were compressed at room temperature at a rate of 2.5 Å^2/molecule/min.

The resulting films are composed of two apparently different molecules as shown in figure 1.

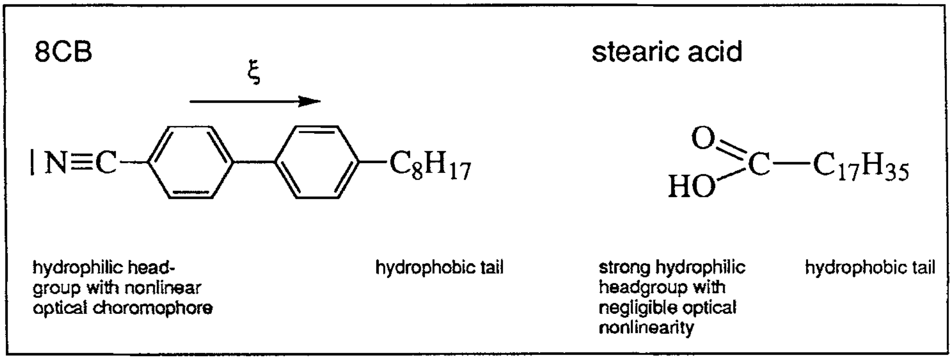

FIGURE 1 Structure and properties of 4-n-octyl-4'-cyanobiphenyl (8CB) and stearic acid.

Stearic acid is composed of a long alkyl chain ($C_{17}H_{35}$) and a carboxylic headgroup (COOH) with strong hydrophobic and hydrophilic properties, respectively. These molecules have a weak optical hyperpolarizibility ($0.07 \cdot 10^{-30}$ esu). The 8CB molecule has a shorter alkyl chain (C_8H_{17}) and a high optical hyperpolarizibility, which is dominated by one element $\beta_{\xi\xi\xi} = 25 \cdot 10^{-30}$ esu, where ξ is the direction of the dipole moment. We can therefore neglect the contribution of the stearic acid and the water surface to the SHG signal [6].

The very different interaction of the molecules with the water surface can be seen in figure 2. This figure presents the surface pressure isotherms for mixed films of 8CB and stearic acid at various mixing ratios from pure stearic acid to pure 8CB:

For pure stearic acid monolayers the surface pressure stays near zero until an area per molecule of 25 Å^2 is reached. Below an area per molecule of 17 Å^2 the slope of the isotherm increases and the monolayer behaves like a solid with low compressibility. The stearic acid molecules are then closely packed and the monolayer can

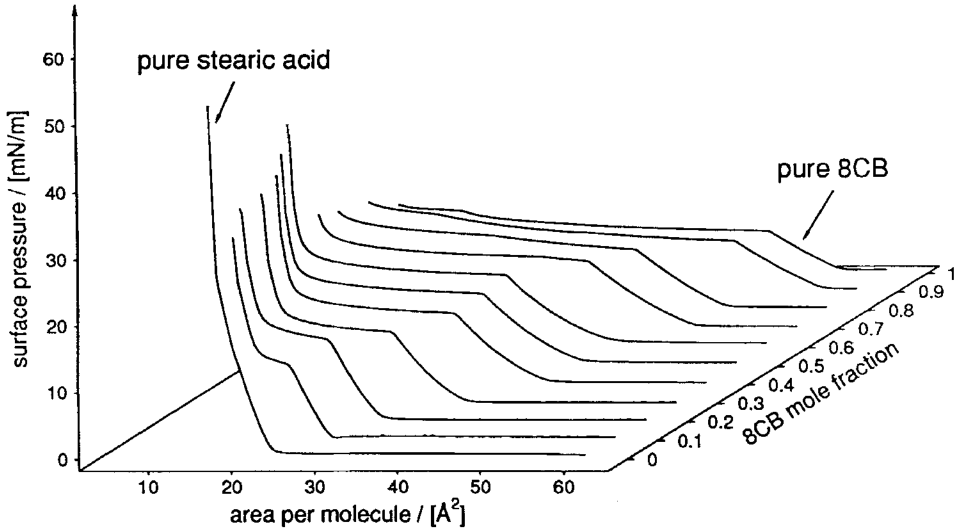

FIGURE 2 Surface pressure isotherms at room temperature for mixed Langmuir films of 8CB and stearic acid at different mole fractions.

be compressed to high surface pressures due to the strong interaction of headgroups with the water surface [7].

The isotherm of the pure 8CB shows an increase in the surface pressure at a much higher area per molecule (48 Å^2), since the inflexible ring systems of the 8CB molecules require a larger area than the carboxylic headgroup of the stearic acid. At an area per molecule of 36 Å^2 the isotherm reaches a plateau at a surface pressure of about 6 mN/m.

For mixed films the plateau becomes narrower and reaches higher surface pressures with decreasing fraction of 8CB molecules. In figure 3a we have plotted the area per molecule at a surface pressure of 5 mN/m and at 25 mN/m as a function of the 8CB mole fraction. The dotted line in the graph is a linear fit of each data set and indicates the correspondence with the additivity rule [9] :

$$A(\pi) = A_1(\pi) \cdot x_1 + A_2(\pi) \cdot x_2 \tag{1}$$

where $A(\pi)$, $A_i(\pi)$ is the area per molecule for the mixed film and the single components respectively as a function of surface pressure π. x_i is the mole fraction of the i-th component.

The additivity rule assumes, that each type of molecule occupies a certain amount of area at a certain π, independent of the other molecules in the film. This means, that each molecular species has the same packing like in its pure film and there is neither a condensation effect nor a steric hindering of the two molecular components.

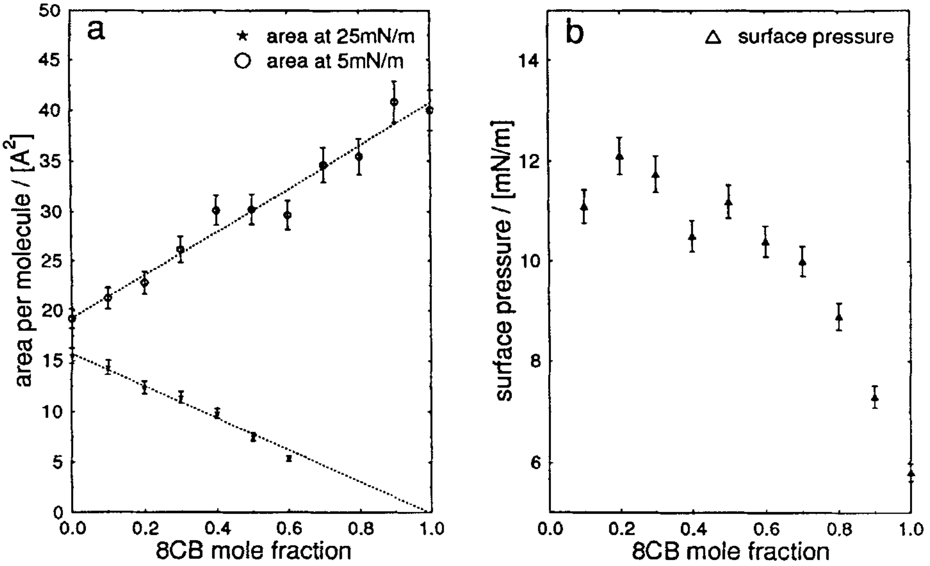

FIGURE 3 (a) Area per molecule at 25 mN/m (stars) and at 5 mN/m (circles). (b) Surface pressure at the beginning of the plateau region in the isotherm.

These conditions can be found for perfect mixing [9] or in the case of immiscible monolayer materials [7].

Another characteristic dataset is given by the values of the surface pressure at the beginning of the plateau as a function of the 8CB mole fraction. As can be seen from figure 3b the surface pressure at the beginning of the plateau in the isotherm increases with the content of stearic acid in the film. A more detailed analysis of these data will be published elsewhere.

SHG MEASUREMENTS

The beam of a Lambda Physics FL2002 dye laser (578 nm, 0.5 mJ per pulse) is focused on the water surface to a spot diameter of 70 μm. The dye laser was pumped by a Lambda Physics EMG102 excimer laser with a repetition rate of 10 Hz and 10 ns pulse duration. The polarization of the fundamental light could be adjusted to any direction by a half-wave plate. After blocking the fundamental wave with a filter, the s- and p-components of the second harmonic light were analyzed by a Glan-Thompson prism. The light was detected in reflection with a Jobin-Yvon HR-320 monochromator, combined with a cooled Hamamatsu R1477 photomultiplier tube.

The geometrical arrangement of the experiment is outlined in figure 4. The fundamental beam with a frequency ω encloses an angle θ_i to the surface normal. The polarization is oriented at an angle α with respect to the plane of incidence (the zy-plane in the laboratory coordinate system xyz). Averaged over the focal spot,

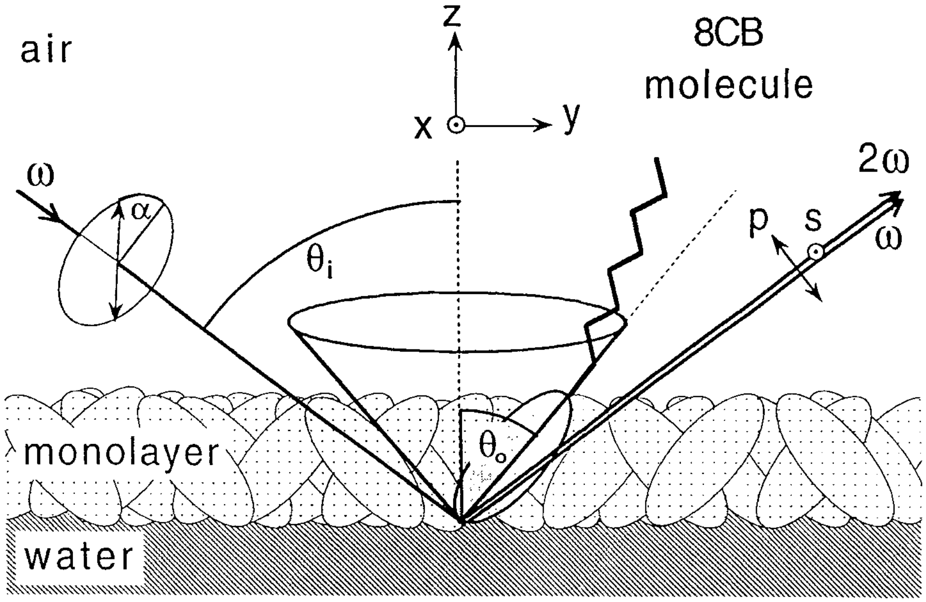

FIGURE 4 Schematic representation of the geometrical arrangement of the experiment.

the 8CB chromophores are randomly oriented along the surface of a cone, including a mean tilt angle θ_0 with respect to the surface normal z. The beam with second harmonic frequency 2ω is reflected in the same direction as the fundamental beam.

The compression process

Figures 5a and 5b display the data from simultaneous measurements of the surface pressure (dotted lines) and the s-polarized SHG signal (triangles) during compression of a pure and a mixed monolayer, respectively. The polarization of the fundamental beam was $\alpha = 45°$. Four different regimes can be distinguished in the compression process:

1. Below a surface pressure of 0.05 mN/m there is no second harmonic generation, indicating that the molecules are in an isotropic phase without polar orientation. Note that the surface pressure is plotted on a logarithmic scale and the fluctuations of the surface pressure in this section are determined by the resolution of the surface balance.

2. When the surface pressure exceeds 0.05 mN/m a first phase transition occurs and the SHG signal increases suddenly and remains constant up to about 0.1-0.2 mN/m. The increase of the SHG signal shows, that here the 8CB chromophores undergo a transition to a polar oriented phase. Note that the surface pressure shows the macroscopic behaviour of the monolayer, whereas the SHG

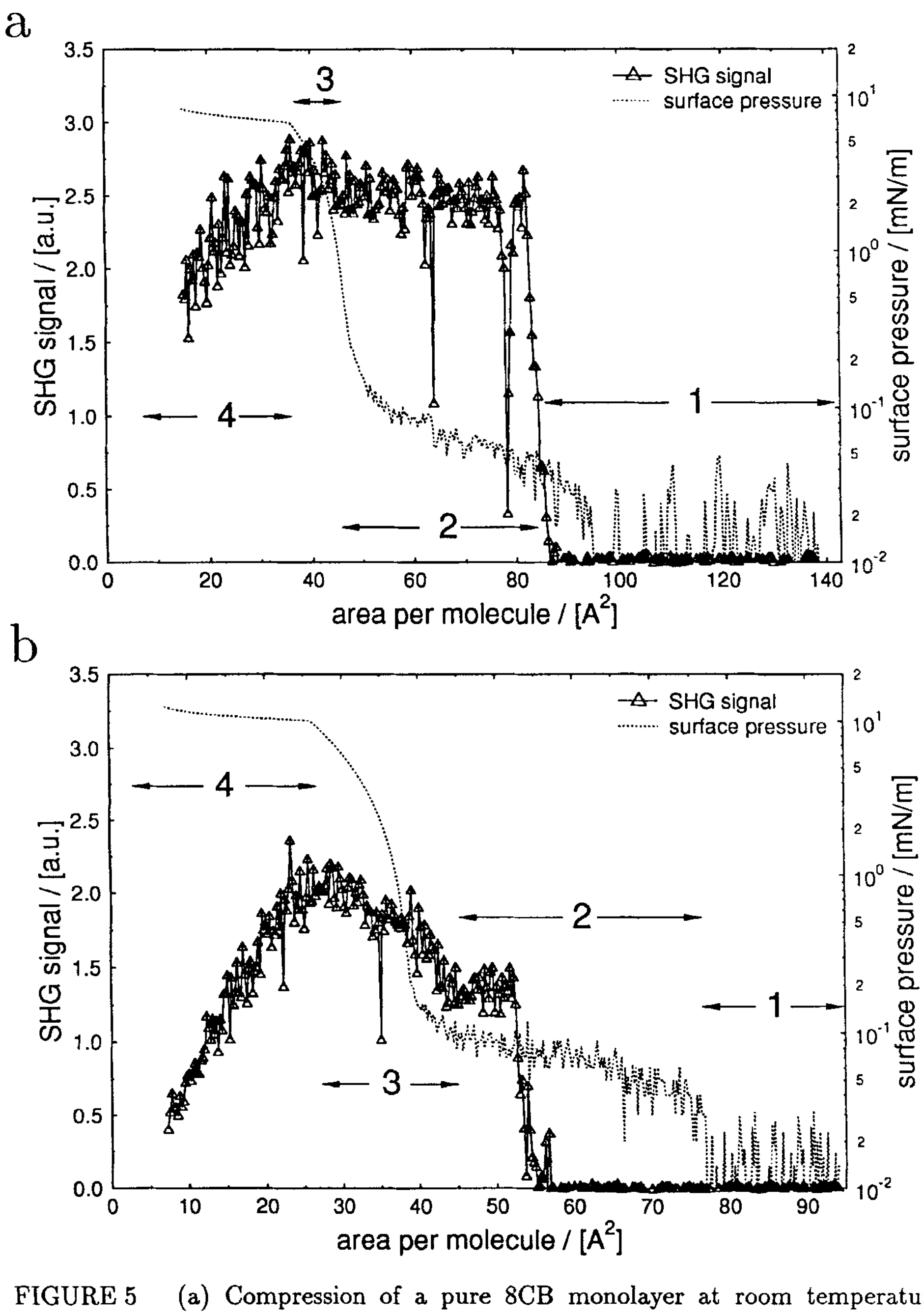

FIGURE 5 (a) Compression of a pure 8CB monolayer at room temperature. (b) Compression of a 1:1 mixed monolayer at room temperature. The dotted lines represent the surface pressure isotherm on a logarithmic scale. The triangles represent the s-component of the SHG intensity recorded simultaneously during compression at 45° polarization of the fundamental light.

signal is related to the orientation of the 8CB molecules in the small area of the focus. Therefore the position where the SHG signal starts to rise in figures 5a and 5b may be arbitrary, depending on the moment when the chromophores are being reoriented just at the focal point. Note that the fluctuations of the SHG signal which occur in this regime exceed the statistical noise. This behaviour of the SHG signal may be interpreted with the coexistence of polar oriented and isotropic patches of the monolayer, a phenomenon which has been observed previously by Xue et al. [8].

3. After all 8CB molecules are polarly aligned, the surface pressure starts to rise due to the increasing repulsion of the molecules. The intensity of the SHG signal shows a slight increase up to a maximum at the beginning of a plateau in the surface pressure isotherm. The maximum is more pronounced for the mixed films (see figure 5b). It is important to recall, that the surface pressure of the mixed films at this maximum is considerable higher than in the pure 8CB films (figure 3b).
4. On further compression in the plateau of the isotherm, the SHG signal decreases. At this point the 8CB molecules begin to rearrange themselves in centrosymmetric manner. A similar behaviour has been reported recently by Xue et al. [8] for pure 8CB films. We have seen, that this collapse is a unique feature for all 8CB films, pure and mixed independent on the mixing ratio. The surface pressure at the edge of the plateau in the isotherm increases with higher mole fractions of stearic acid molecules (see figure 3b) and thus is a figure of merit for the stability of the 8CB molecules in the film, and we may conclude that the presence of the stearic acid molecules stabilizes the 8CB molecules.

Polarization dependent SHG measurements

Due to the uniaxial symmetry of the monolayer and Kleinman's symmetry there are only seven nonvanishing elements in the χ-tensor which describes the nonlinearity of the monolayer [6]. These elements are:

$$\chi_{zii} = \chi_{izi} = \chi_{iiz} = \frac{1}{2} \cdot N_s \cdot \sin^2\theta_0 \cdot \cos\theta_0 \cdot \beta_{\xi\xi\xi} \qquad i = x, y \tag{2}$$

and

$$\chi_{zzz} = N_s \cdot \cos^3\theta_0 \cdot \beta_{\xi\xi\xi} \tag{3}$$

where

N_s = surface density of the molecules,

$\beta_{\xi\xi\xi}$ = molecular hyperpolarizibility.

From equations 2 and 3 a simple expression for the molecular tilt angle θ_0 can be obtained:

$$\theta_0 = \arctan\left(\sqrt{2\chi_{zxx}/\chi_{zzz}}\right) \tag{4}$$

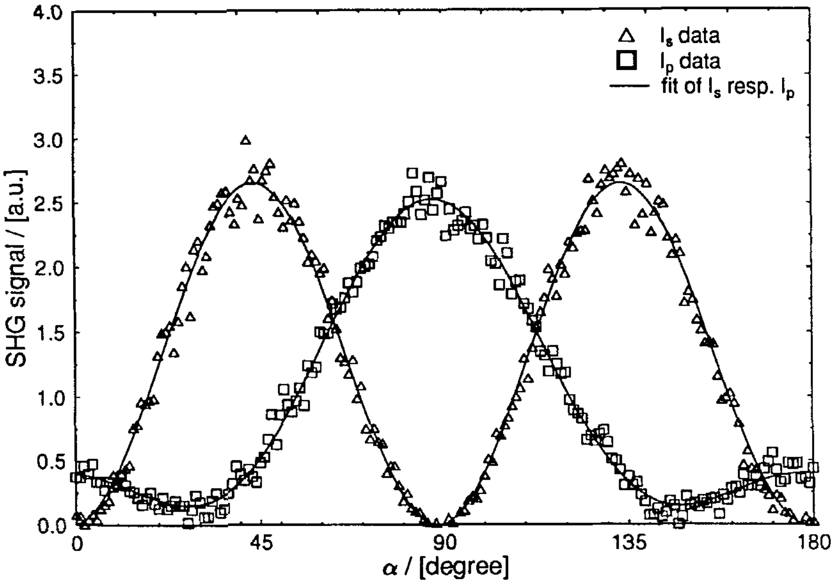

FIGURE 6 SHG signal for a pure 8CB monolayer at a surface pressure of 2.1mN/m as a function of fundamental polarization α. The two traces △ and □ are the s- and p-components of the second harmonic intensity. The solid lines represent fits of the theoretical expressions given by the square of equation 5.

A relation between the p- and s-components of the second harmonic wave and the polarization of the fundamental field has been derived by Zhang et al. [10] :

$$\begin{aligned} E_p &= \left(A \cdot \cos^2\alpha + B \cdot \sin^2\alpha\right) \cdot E^2 \\ E_s &= H \cdot \sin(2\alpha) \cdot E^2 \end{aligned} \tag{5}$$

Here A, B and H are functions of the dielectric constants of the media at ω and 2ω, the χ-tensor of the monolayer and the angle of incidence of the fundamental light. E is the amplitude and α is the polarization of the fundamental electric field.

Figure 6 shows the s- and p-polarized SHG intensity reflected from a pure 8CB monolayer at a surface pressure of 2.1 mN/m as a function of α. The solid lines represent fits of the theoretical expressions for the p- and s-polarized SHG intensity given by the square of equation 5. The results of the fit were used to determine $\theta_0 = 57.9°$.

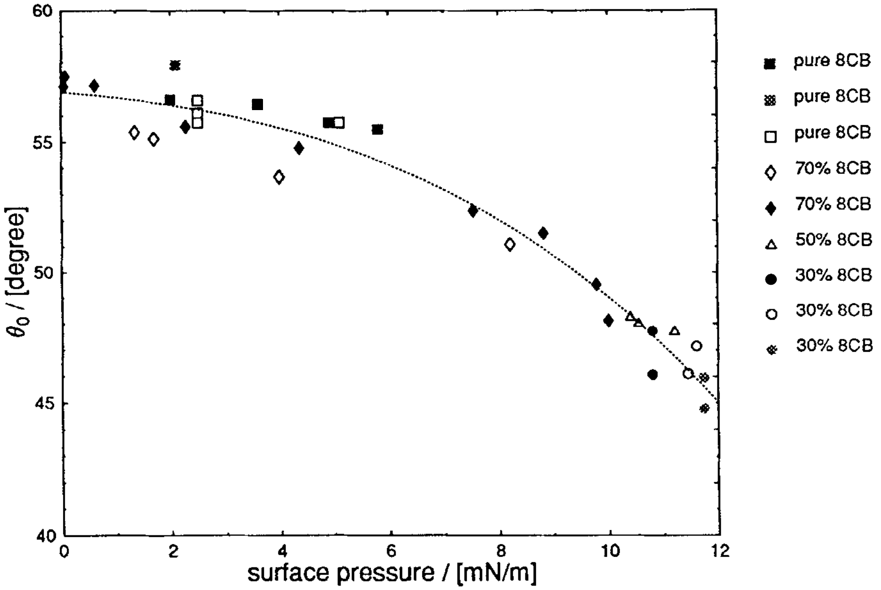

FIGURE 7 Tilt angle θ_0 of the 8CB molecules in pure and mixed monolayers as a function of surface pressure. In the mixed films higher surface pressures can be achieved, hence the the 8CB molecules can be aligned in a more upright position.

In the same way we have analyzed the mixed films. The result, the tilt angle as a function of surface pressure is given in figure 7. The measurements were repeated several times at each mixing ratio. In the plotted graph each type of marker denotes an individual monolayer. The data show how the 8CB molecules are being aligned in a more upright orientation with increasing surface pressure. A striking result is, that the orientation of the 8CB molecules only depends on the surface pressure and not on their concentration in the film.

CONCLUSIONS

The compression process of both pure and mixed monolayers of 8CB can be divided into four regimes (see figure 5a and 5b):

Starting from a non polar orientation of the 8CB chromophores at zero surface pressure (regime 1) the first transition leads to a polar oriented phase of the 8CB (regime 2). With steadily increasing surface pressure this polar phase is further compressed, which results in a simultaneous decrease of the tilt angle θ_0 of the 8CB chromophores (regime 3). This means that the 8CB molecules are reoriented in a more upright position. Finally the 8CB molecules undergo a transition to a centrosymmetric arrangement (regime 4).

In the mixed films the presence of the stearic acid molecules stabilizes the 8CB molecules but there is no condensation or steric hindering observed. It is interesting to note, that this effect shifts the final phase transition which leads to a centrosymmetric alignment of the 8CB molecules to considerable higher surface pressures. Our experimental results show, that the orientation of the 8CB molecules only depends on the surface pressure and not on their concentration in the film. Since higher surface pressures can be achieved in the mixed films, the 8CB molecules can be aligned in a more upright orientation.

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