

How do smectic liquid crystals of different molecular length mix in thin films?

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Abstract. We present a model for the structure of binary mixtures of smectic compounds in freely suspended films of 2–7 layers. The compounds are the hexyl (6AB) and dodecyl (10AB) homologues of *p,p'*-dialkylazoxybenzene that differ by about 40% in molecular length. X-ray reflectivity indicates that no demixing occurs between 6AB and 10AB molecules, while also there is no indication found of increased roughness at the film surfaces. However, the surface layers are somewhat expanded compared to the interior layers. This can be explained by backfolding of the dodecyl end chains of 10AB molecules at the surface *via* two *gauche* kinks, which ensures dense packing. This model is supported by surface tension measurements that indicate an increased amount of alkyl groups at the surfaces.

PACS. 61.10.Kw X-ray reflectometry (surfaces, interfaces, films) – 61.30.Cz Molecular and microscopic models and theories of liquid crystal structure – 61.30.Hn Surface phenomena: alignment, anchoring, anchoring transitions, surface-induced layering, surface-induced ordering, wetting, prewetting transitions, and wetting transitions

1 Introduction

The smectic-A phase of liquid crystals can be described as a one-dimensional stack of liquid layers consisting of orientationally ordered elongated molecules [1]. It is particularly interesting from a structural point of view as a model system of low-dimensional ordering [2,3]. Another remarkable example of spontaneous organization of smectics is found in binary mixtures of molecules with different dimensions. Smectic-A mixtures show complete miscibility in effectively all cases, even if the mesogens differ by more than 40% in length [4–7]. This nearly universal miscibility is important for applications of liquid crystals because usually the desired material properties can most easily be achieved in mixtures. It can be contrasted with solid solutions in which the components demix if the molecular lengths differ more than about 15% [8,9]. The variation with concentration of the layer spacing of a smectic mixture is in close agreement with the weight-averaged layer thickness of the components [10]. The molecules of both compounds are incorporated statistically into the same

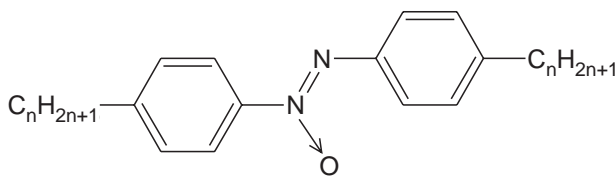
layer: they are distributed with equal probability around the plane of the average positions of the centers of mass. Hence, the quasi-long-range order of the density modulation parallel to the layer normal is not altered in mixtures. Of course, this process of maintaining the density is of a highly dynamic nature.

The situation described applies to approximately symmetric rod-like molecules. For mixtures of such molecules with strongly terminally polar ones, strong deviations from linearity are observed. These can be attributed to the anti-parallel association of the polar compound, whose equilibrium is distorted upon mixing. Other cases that deviate from the additivity rule comprise branched molecules and systems with hydrogen bonds. For a discussion of these aspects we refer to reference [10]. In this paper we address the question whether the mixing behavior can be influenced by means of external factors, such as surfaces. The presence of a surface necessarily distorts the symmetry around the centre of the smectic top layer. We have chosen thin smectic films, that can be freely suspended over a hole in a substrate, as a model system to investigate binary mixing of smectics of different molecular length near surfaces. Even in two-layer films we still observe full mixing. A model is given that accounts for the local packing in this situation, which is substantiated by measurements of the surface tension.

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n=8:	K 39.1	Sm-A 63.9	N 66.2	I
n=6/10:	K 35-38	Sm-A 53-60	N 62-64	I

Fig. 1. Molecular structure of the n AB series of compounds. Phase transitions (in degree centigrade) are given for $n = 8$ and the equal molar mixture of $n = 6$ and $n = 10$.

2 Experimental

We used equal molar amounts of compounds 6AB and 10AB from the p,p' -dialkylazoxybenzenes, abbreviated as n AB [11], where n indicates the number of carbon atoms in the alkyl chain (see Fig. 1). The core of the phenyl rings can be regarded as approximately rigid with an average width of about 0.5 nm, while the alkyl chains are flexible. All-*trans* stretched 6AB and 10AB molecules have a length of 2.4 nm and 3.6 nm, respectively. In spite of this difference of approximately 40%, in the bulk full mixing occurs. For equal molar amounts of the components one would expect the behavior of the mixture to be very similar to that of 8AB. Films of 2, 3, 4, 5 and 7 layers of both the mixture and 8AB were spanned over a rectangular knife-edged hole in a stainless-steel holder. The films covered an area of about $10 \times 25 \text{ mm}^2$. The holder was placed vertically in an oven, temperature controlled to within 0.1 °C, and subsequently evacuated to $< 10^{-2} \text{ Pa}$. For further details we refer to Mol *et al.* [12].

The films were investigated by specular X-ray reflectivity at 40 °C after equilibration for about 12 hours. Copper $K\alpha 1$ -radiation from a rotating anode X-ray generator (Rigaku RU-300H) was used (wavelength $\lambda = 0.154 \text{ nm}$). The beam was collimated by a parabolic graded multilayer mirror and a pre-sample slit of 0.1 mm. At specular reflectivity the momentum transfer $\mathbf{q} = \mathbf{k}_{\text{out}} - \mathbf{k}_{\text{in}}$ is perpendicular to the air-film interface (z -direction), *i.e.* $|\mathbf{q}| = q_z$. Hence, the reflected intensity is sensitive to the electron density profile in the latter direction, averaged over the footprint of the incident beam. The density profile was determined by comparing calculated and experimental reflectivities. Calculations were based on a parametrized molecular model in which each smectic layer is approximated by a box-like function, convoluted with a Gaussian probability density to take the fluctuations into account [12]. The best-fit curve to the data was determined by a minimization procedure; each set of data was fitted independently.

Additional measurements of the surface tension of the films were performed using a method developed by Huang and coworkers [13]. In short, a film is spread across a rectangular opening in a plate, the plane of which is vertical. An approximately 40 μm diameter surgical suture sus-

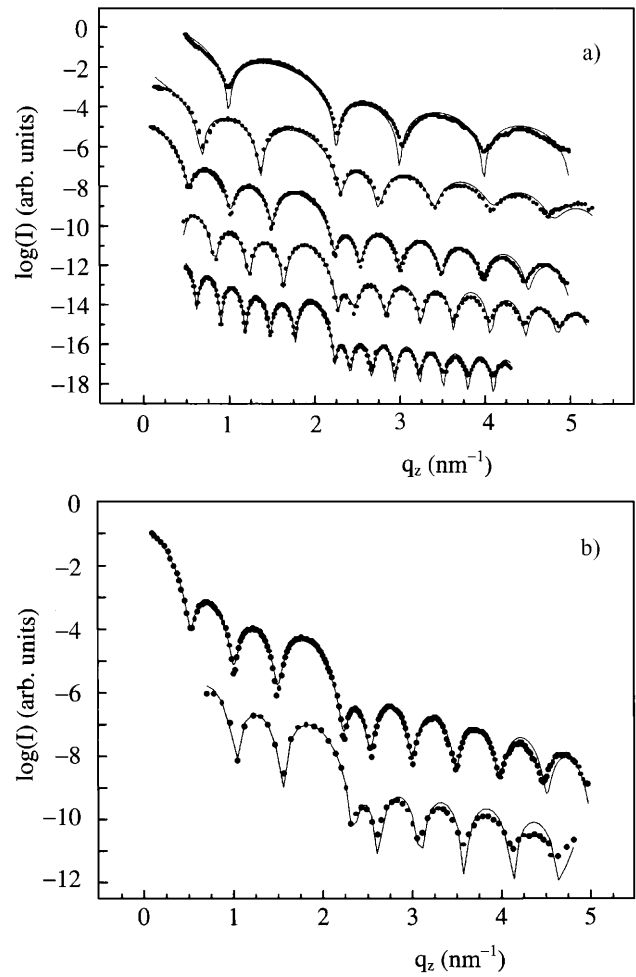


Fig. 2. X-ray reflectivity results and their fits. a) Films of 2, 3, 4, 5 and 7 layers of the 6AB/10AB mixture; the curves are shifted vertically for clarity. b) Comparison of a 4-layer film of the mixture (upper curve) and of 8AB (lower curve).

Table 1. Observed variation of $(d_{\text{mix}}/d_{8\text{AB}} - 1)$.

# layers	All layers	Interior layers	Surface layers
2	3.7 %	–	3.7 %
3	2.6 %	2.0 %	3.0 %
4	3.8 %	0.7 %	6.9 %
5	3.3 %	2.0 %	5.0 %
7	1.6 %	1.7 %	1.3 %

pends a small, known mass and spans the opening of the plate. The suture is guided by a V-groove and clamped in place at the plate's upper end. The film is bounded at one side by the suture, which is deformed into an arc because the surface tension causes the film to minimize its surface area. The radius of curvature can be measured and thus the surface tension determined. Results for several classes of liquid crystals, including the n AB series, have been summarized by Mach *et al.* [14].

Table 2. Values for the average surface tension of the 6AB/10AB mixture for various thickness films.

# layers	2	3	4	5	6	7	8
γ (mN/m)	25.37	25.44	25.47	25.46	25.35	25.42	25.48

**Fig. 3.** Cartoon model for a mixture of 6AB and 10AB molecules at a surface (at the left), indicating an increased exposure of $-\text{CH}_2-$ groups.

3 Results

Figure 2a) shows experimental reflectivity curves for films of 6AB/10AB of 2, 3, 4, 5 and 7 layers, together with the fitted reflectivity. Figure 2b) shows a comparison of the reflectivities of 4-layers films of the 6AB/10AB mixture and of 8AB. The results from the fits are summarized Table 1. From these data we can reach the following conclusions:

1. The fitting procedure converges for all data sets to a mixed model. Any attempt to fit to a model of phase-separated 6AB and 10AB does not work.
2. Comparing films of the mixture and of 8AB, we note a significant difference in the total film thickness (in absolute terms varying from about 0.2 nm for a 3-layer film to about 0.5 nm for a 4-layer film).
3. The difference in total film thickness can be attributed to the surface layers d_{surf} ; in contrast, the interior layers d_{int} of the mixture and of 8AB do not differ much. Compare the corresponding values of $(d_{\text{mix}}/d_{8\text{AB}} - 1)$ in Table 1.
4. The rms fluctuation amplitude σ at the two air-film interfaces shows no significant difference comparing films of the mixture to 8AB. Both for 3- and 4-layer films of 8AB we find $\sigma = 0.32$ nm; the corresponding values for 6AB/10AB are $\sigma = 0.30$ nm and $\sigma = 0.36$ nm, respectively. Hence, within the experimental variation the surface roughness is in both cases very similar.

Finally, Table 2 shows the surface tension γ for films of 6AB/10AB in the range of 2 to 8 layers. The mean value is $\gamma = (25.43 \pm 0.10)$ mN/m, while there is no significant dependence on the film thickness. The surface tension for 8AB films has been reported earlier to be 24.3 mN/m [14]. Hence, the 6AB/10AB mixture has a significantly larger surface tension than 8AB.

4 Discussion

Decisive arguments indicate that no demixing occurs in the films of the binary mixture 6AB/10AB. First, comparing the X-ray reflectivity of three- and four-layer films

of the mixture with the corresponding 8AB films, we note a good resemblance, which means that the additivity rule for binary mixtures is approximately fulfilled. Second, fitting the experimental curves results in convergence to the mixed state model for all data sets.

Qualitatively, the structure of films of the binary mixture can be described as follows. To accommodate molecules of different length within the smectic layered structure, the molecules are statistically distributed, similarly as in the bulk. However, at the surfaces such a structure would lead to a loose packing of the outer 10AB tails, or in other words, to increased roughness on a molecular scale. Moreover, as the smectic order promotes close packing of the aromatic centers of neighbouring molecules, this would introduce an extra asymmetry around the center plane of the smectic surface layers. The experiments show no indication of any of these effects. A possible way out is to assume that at the surfaces there is back-folding of the end chains of 10AB molecules adjacent to 6AB molecules. This requires a change in conformation of the flexible dodecyl chains from an all-*trans* state to a state with two *gauche* kinks as schematically indicated in Figure 3. Though energetically somewhat less favourable, such a situation promotes a close packing and minimizes the surface area. Nevertheless, the packing will necessarily still be somewhat less dense than can be accomplished for 10AB chains in the bulk of the mixture or for 8AB chains at a surface. This explains why in the mixture the surface layers are thicker than the interior ones, in contrast to the situation for 8AB. Though these arguments apply locally, they can —averaged over a large region— account for the overall structure of the film as derived from the experiments.

The model given is supported by the surface tension measurements. Mach *et al.* [14] investigated the dependence of γ on specific terminal groups. In fact the surface tension is rather determined by the molecular groups exposed at the surface than by the entire molecule itself [15]. A free surface populated exclusively by $-\text{CH}_3$ terminal groups leads to $\gamma \simeq 20$ –21 mN/m, which increases to 30–31 mN/m for $-\text{CH}_2-$ groups. For a mixed

surface population roughly a weighted average of these two values can be expected. Hence the increase in γ , observed in going from 8AB to the 6AB/10AB mixture, can be interpreted as a shift to less $-\text{CH}_3$ terminal groups and more $-\text{CH}_2-$ groups exposed at the surfaces. This is exactly what is expected upon introduction of *gauche* kinks in 10AB molecules (see Fig. 3).

We conclude that in thin freely suspended films of 6AB/10AB mixtures no demixing occurs. The presence of a surface increases the thickness of the top layer, while the higher surface tension (compared to 8AB films) suggests that more alkyl groups ($-\text{CH}_2-$) are present at the surface. The experiments can be explained by a conformation of 10AB molecules at the surface with the dodecyl end chain backfolded by means of two *gauche* kinks.

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