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Layering Transitions and Reentrant-Like Phenomenon in Thin Films of Three-Block Organosiloxane Smectogens at the Air/Water Interface

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Abstract. — The surface pressure induced layering transition of three-block amphiphilic smectogens at the air/water interface is observed and characterized by film balance measurements, Brewster angle microscopy and X-ray reflectivity. Since the systems possess a fluid smectic A bulk phase the transition is reversible with little hysteresis and occurs layer by layer. Whereas the monolayer at the air/water interface exhibits polar smectic C-like order the multilayer is in a smectic A arrangement equivalent to that in bulk. The reentrant-like transition can be ascribed to a loss of order of water surrounding the hydrophilic head when removing molecules from the water surface. The thickness uniformity and stability may be ascribed to the line tension related to a domain boundary and to long-range van der Waals forces between interfaces. The mono- as well as multilayers can be transferred onto solid substrate apparently without any major structural changes.

1. Introduction

The interactions of a surface with an adjacent layered material are of high interest from a fundamental research as well as from a technological point of view [1]. Of special relevance for basic studies in this field are smectogens on water surfaces. The water surface is smooth, unstructured, its chemical potential can be varied *via* additives, and the smectogens may respond sensitively to external forces due to their polymorphisms. With a hydrophilic group attached, smectogens can be anchored at the water surface. If this group is not too hydrophilic layering transitions can be induced *via* density changes. These transitions are probably favored by the fluidity of the mesophase and the natural tendency of the molecules to form smectic layers.

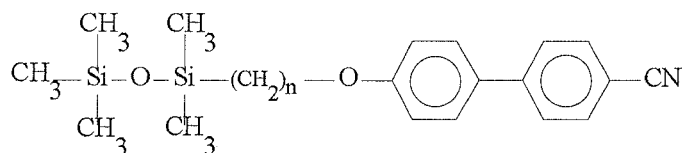
Previous studies on pressure induced layering transitions have used molecules with weakly hydrophilic groups [2,3] and alkylated mesogens. However, the thermodynamics and reversibility were difficult to control since the bulk material tended to crystallize. Multilayers have also been observed and investigated using molecules containing cyano groups [4–7]. In this case crystallization also occurs for films containing more than three layers [4].

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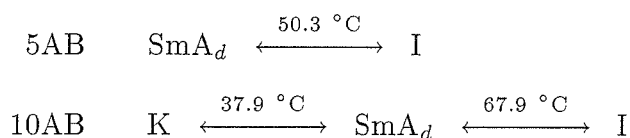
We avoid crystallization by using molecules with a third siloxane block. With these molecules reversible formation of discrete multilayers is observed. We prove the existence of reentrance from a smectic C to a smectic A phase and give structural details. The floating multilayers can be transferred on solid substrates for more detailed experiments.

2. Experimental

The compounds were synthesized and characterized following the method described in the literature [8] and furthermore purified by HPLC. The full chemical formula abbreviated in the following as nAB (n the number of CH_2 groups in the aliphatic part) is:



These compounds exhibit a fluid smectic A_d phase at low temperature and a liquid isotropic one at high temperature [9]. The corresponding thermotropic bulk behavior is:



The smectic period of the bulk material ($d_{5AB} = 36.4 \text{ \AA}$ and $d_{10AB} = 49.6 \text{ \AA}$) is between one and two molecular lengths ($l_{5AB} = 22.6 \text{ \AA}$ and $l_{10AB} = 28.7 \text{ \AA}$) [9]. The molecules are arranged within the layers with a partial overlapping with a certain degree of head to head association of the molecules through their cyano endgroups [10].

The pressure/area isotherms were recorded with a commercial automatic Lauda film balance. The temperature and the pressure of the Langmuir trough were controlled to an accuracy of 0.2°C and 0.2 mN/m .

The monolayers were spread on pure water (Millipore, $18.2 \text{ M}\Omega\text{cm}$) from chloroform solutions (1 mMol). The compounds and their spread monolayers were insoluble in water. There was no decrease in the film pressure as long as the spread monolayers were kept at a constant surface area of about 50 \AA^2 for more than 20 hours. The effect of the solvent was examined by alternatively using ether. No appreciable difference was detected. The isotherms were recorded at low compression rate of about $0.1 \text{ \AA}^2/\text{s}$ or less. High compression rates cause deviation of the plateau from the horizontal, affects the isotherms when undergoing multilayer formation and also affects the reversibility of the process. Obviously equilibrium is not reached at high speed.

Silicon wafers with naturally grown oxide layers were used as solid substrates. Their surfaces were prepared hydrophilic according to a modified RCA method [11], kept under water, and used within less than 2 hours. The floating mono- and multilayers were transferred onto the SiO_2 surface at 10 mN/m and 16 mN/m , respectively, at a dipping speed of 5 mm/min .

Specular X-ray scattering was performed with a commercial $\theta/2\theta$ instrument (STOE & CIE GmbH Darmstadt, $U = 40 \text{ kV}$, $I = 30 \text{ mA}$, $\lambda = 1.54 \text{ \AA}$ ($\text{CuK}\alpha$)). The divergence of the incoming beam was 0.1° , the 2θ resolution was 0.05° . The analysis of the X-ray data was performed with a Box-model using the software described elsewhere [12].

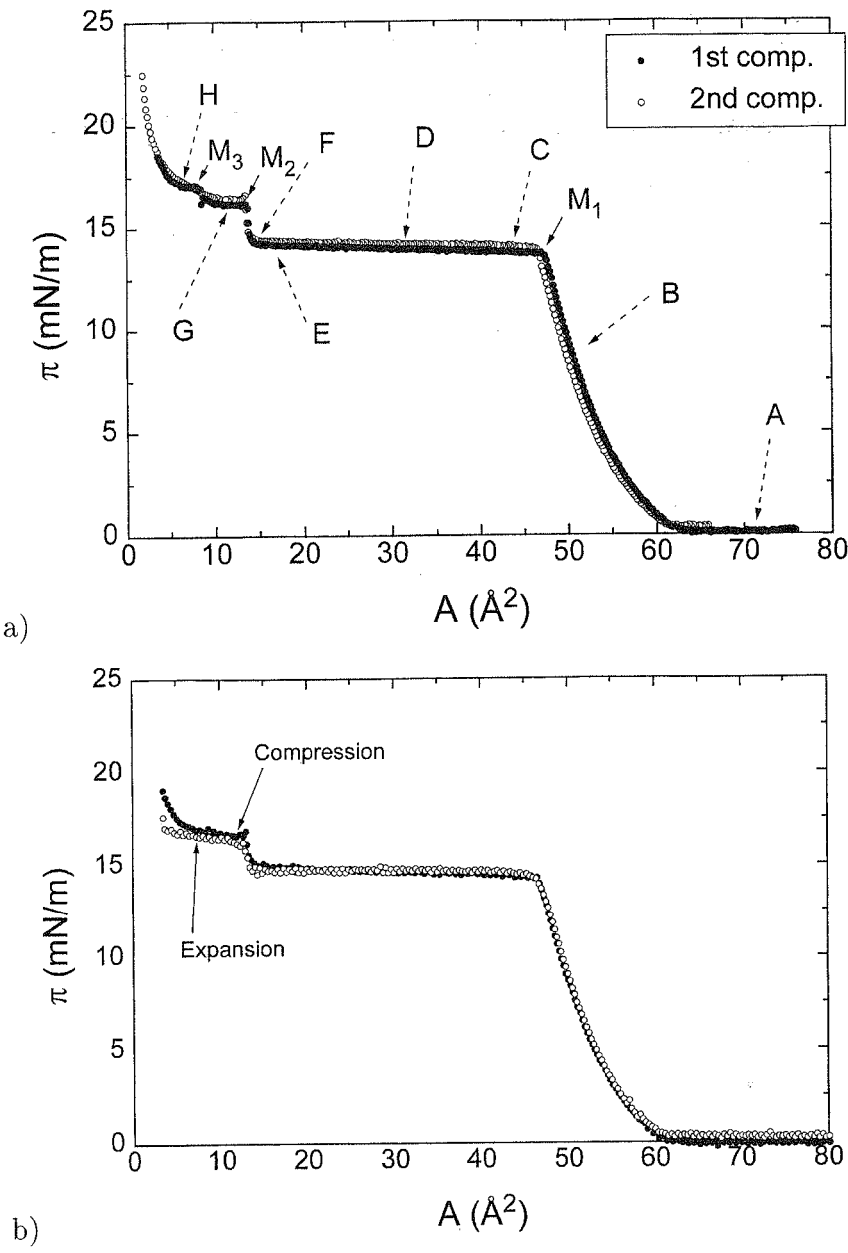


Fig. 1. — Typical $\pi - A$ isotherms at the Air-Water interface for 5AB a) on compression and b) both on compression and expansion.

The Brewster Angle Microscope (BAM, NFT Göttingen) was mounted on a Langmuir film balance from R&K (Wiesbaden, D). The spacial resolution of the method is about 4 μm . Experimental details of the BAM are described elsewhere [13,14]. The images were corrected for geometric distortion due to the observation at the Brewster angle (53.1°).

3. Results and Interpretation

Figure 1 shows a typical pressure/area isotherm for the most suitable system for our study, 5AB. One observes sharp breaks of the isotherm slopes, followed by horizontal parts at molecular areas M_1 , M_2 and M_3 , and there are no quantitative differences comparing the first and the

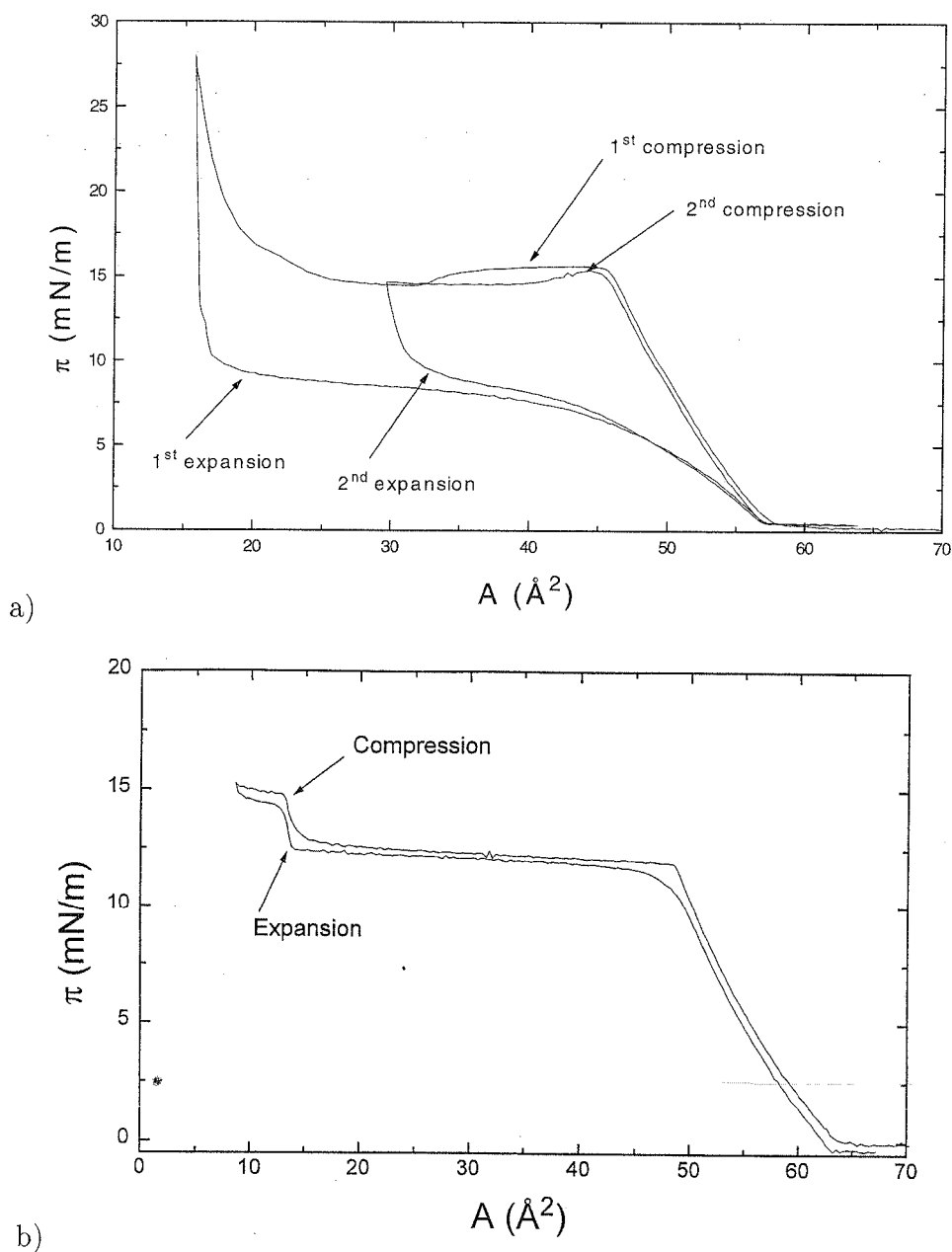


Fig. 2. — Isotherms of compound 10AB both on compression and expansion at a) 5 °C and b) 45 °C.

second compression (Fig. 1a). Also, at least comparing M_1 and M_2 and the pressure of the horizontal part (14.5 mN/m) there is no strong hysteresis (Fig. 1b). The breaks suggest a successive multilayer formation.

The situation is more complex for 10AB (Fig. 2). Up to room temperature there is a strong hysteresis, and first and second compression deviate somewhat in the horizontal range (Fig. 2a). Apparently multilayer formation has to be nucleated, indicative of an ordered film. At high temperature (above ≈ 30 °C), the 10AB compound behaves like 5AB (Fig. 2b).

Since for 5AB the reversible layering transitions were observed within the whole temperature range examined (5 – 60 °C), the thermodynamics could be investigated *via* temperature dependent studies. Figure 3a shows that the transition pressure is reduced upon increasing the temperature whereas the molecular areas M_1 , M_2 are virtually constant. The reduction occurs

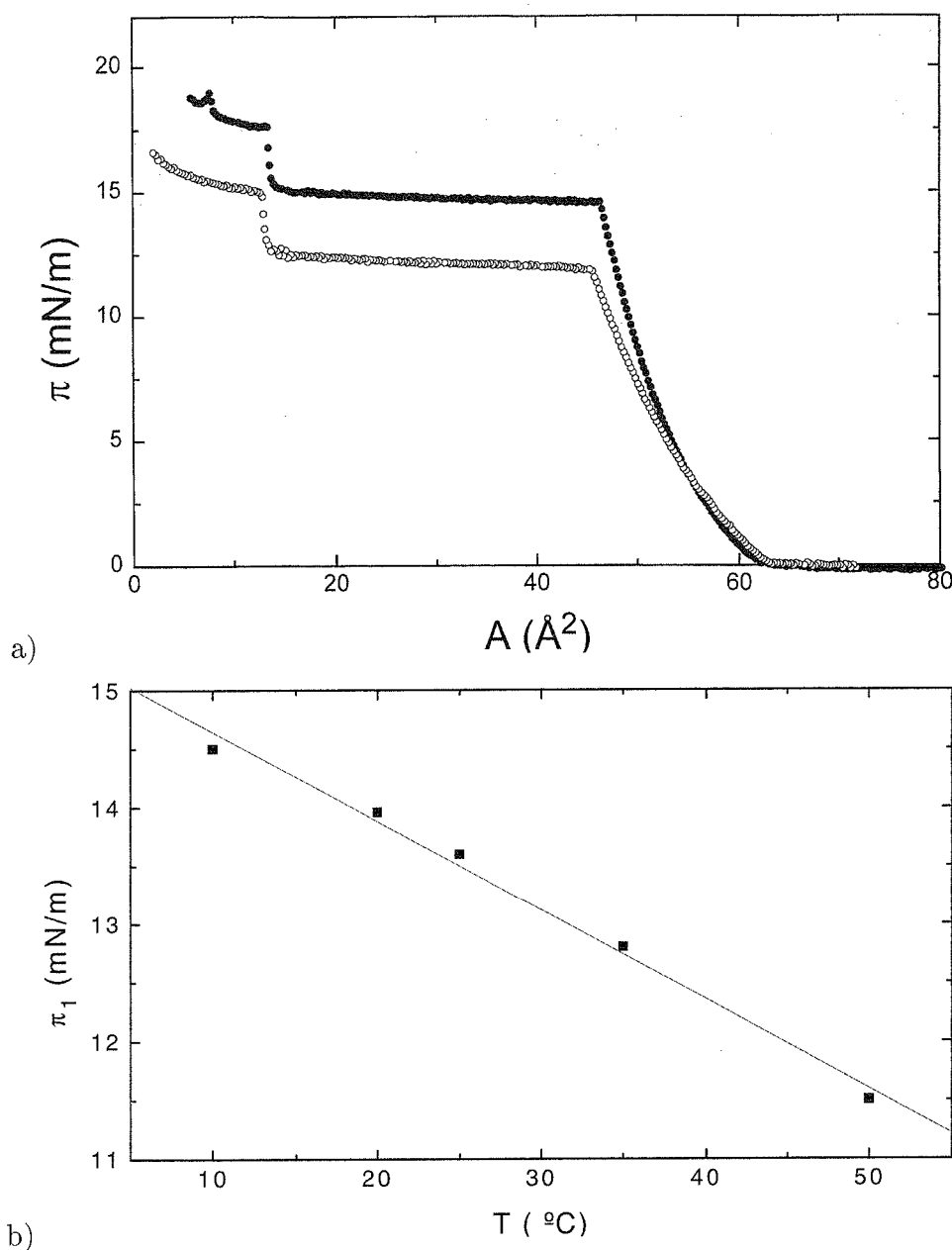


Fig. 3. — a) Temperature effect on the $\pi - A$ behavior of 5AB: isotherms at 5 °C (filled squares) and at 50 °C (opened squares); and b) variation of the plateau pressure at M_1 with temperature.

linearly with temperature (Fig. 3b) with a slope $\frac{d\pi_c}{dT} = -0.08 \frac{\text{mN}}{\text{m K}}$. This behaviour is rather unusual and indicates the establishment of disorder upon compression. This behaviour is observed as reentrant phenomenon in thermotropic liquid crystals ($S_A - S_C - S_A$) and has also been observed in thin film of HOBACPC at the air/water interface [2] and will be discussed below. Since here the phase of lower order at higher pressure is not the original one we call the phenomenon reentrant-like.

More detailed information on film structure and lateral homogeneity is obtained by Brewster Angle Microscopy (BAM) as shown in Figure 4. For very low surface pressure one observes dense liquid phase spots in equilibrium with a gas phase forming polygon patterns, mainly

Table I. — *Fit parameters of the experimental data with two-box model.*

Monolayer	siloxane sublayer	aromatic-paraffinic sublayer
Thickness Å	5.0	9.7
density $e/\text{\AA}^3$	0.38	0.45
Air/Film roughness Å	4.5	
Multilayer	upper layer	aromatic-paraffinic sublayer
Thickness Å	40.3	10
density $e/\text{\AA}^3$	0.33	0.47
Air/Film roughness Å	4.4	

hexagons (foam phase) (4A). In the range of increasing surface pressure below M_1 , one observes bright areas with smooth boundaries (4B). This Schlieren texture is also observed with free-standing smectic C films [15] and is due to the continuous variation of the tilt azimuth. Hence this picture proves smectic C like ordering, *i.e.* a uniform molecular tilt. Upon increasing the pressure into the first plateau beyond M_1 one observes bright spots due to nucleation of a top layer (4C). On further compression these areas increase in size (4D,E). In addition when two circular domains coalesce, the shape of the resulting domain relaxes rapidly to a circular one due to the fluidity of the system and a large line tension contribution. The uniform brightness of all domains indicates uniform thickness. The absence of Schlieren textures indicates the absence of smectic C like ordering, *i.e.* no in-plane anisotropy. The absence of in-plane anisotropy, at least on a mesoscopic length scale, can also be deduced from the fact that rotation of the analyzer did not cause variations in brightness within each domain as observed in the case of other amphiphiles (see for *e.g.* Refs. [16,17]). On further compression these domains deform and cover the surface almost completely (4F). Beyond M_2 a third layer (4G) and then a fourth layer (4H) are formed.

The floating mono- and multilayer could be transferred onto solid substrates. The X-ray reflectograms (Fig. 5) show pronounced maxima and minima indicating high thickness uniformity. For a quantitative analysis we used a box-model considering the monolayer as a slab containing the siloxane backbone on top and all other regions in a slab closer towards the substrate. Table I shows the result of the fit analysis (Fig. 5a). The consistency of this fit is checked by comparing the electron number expected from the chemical formula for the siloxane group (83) with the one calculated from the fit. With a molecular area of $A_{\text{si}} = 46 \text{ \AA}^2$, a density $\rho_{\text{si}} = 0.38 e/\text{\AA}^3$ and $l_{\text{si}} = 5.0 \text{ \AA}$ one derives $N_{\text{si}} = 87$, in close agreement with the expected value. The overall thickness of the monolayer (14.6 \AA) is well below that expected for the stretched molecule oriented normally to the surface (22.6 \AA). This indicates the existence of a tilt and, assuming a rod-like molecule, we can estimate the tilt angle θ according to $\theta = \arccos(14.6/22.6)$ and obtain $\theta \cong 50 \text{ deg}$.

The multilayer transferred at $\cong 16 \text{ mN/m}$ can be approximated by one thick layer on top of the aromatic-paraffinic layer, in contact with the substrate, with fit parameters in Table I and fitted curve in Figure 5b. Of special relevance is the overall thickness which is derived

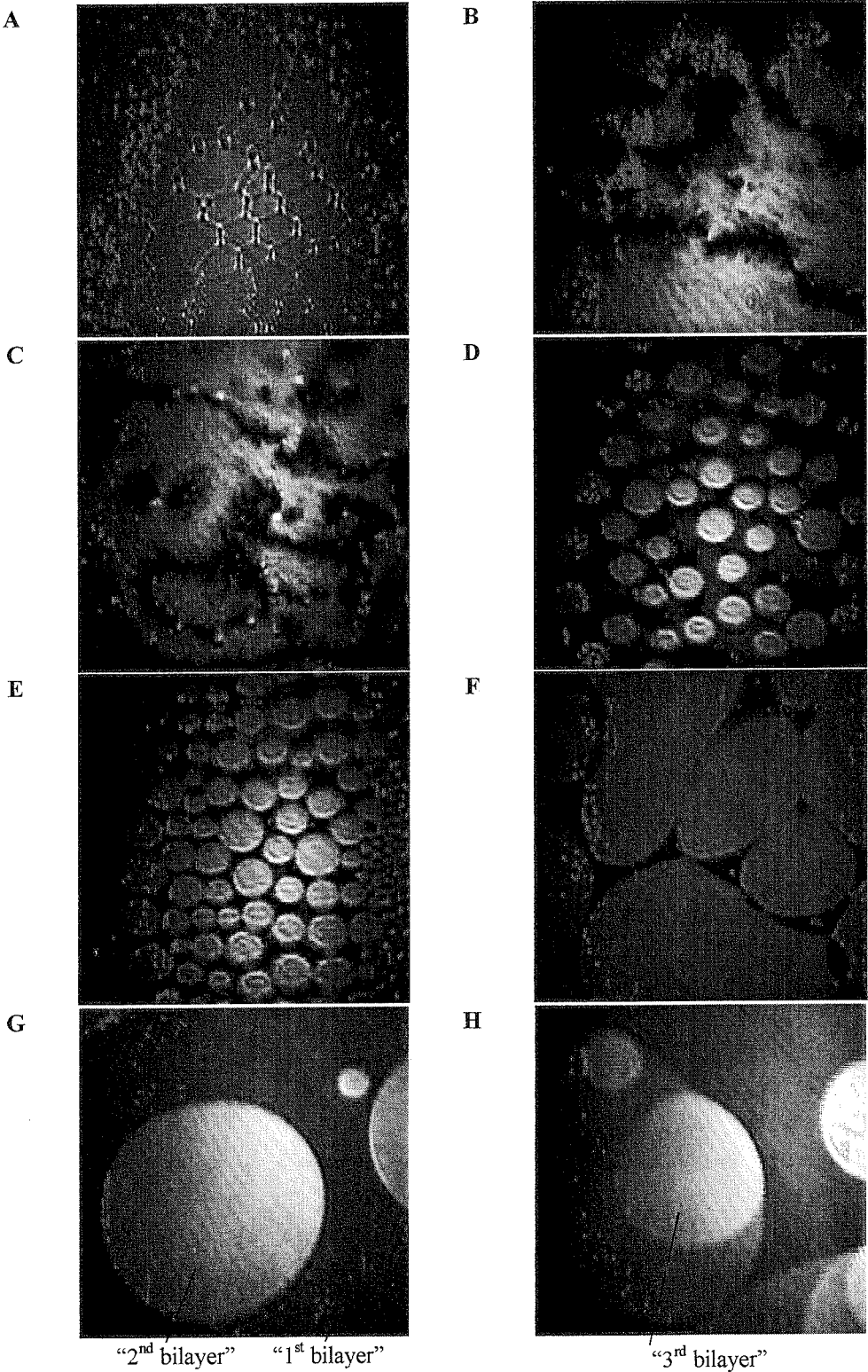


Fig. 4. — Brewster Angle microscopy textures: A) Condensed monolayer/gas coexistence at zero pressure, B) Schlieren texture in the monolayer, C) Nucleation spots of the second layer “1st bilayer” and D), E), F) their continuous growth with compression. G) Growth of the third layer “2nd bilayer” and H) growth of the fourth layer “3rd bilayer” and overlapping of multilayer domains near the bulk collapse.

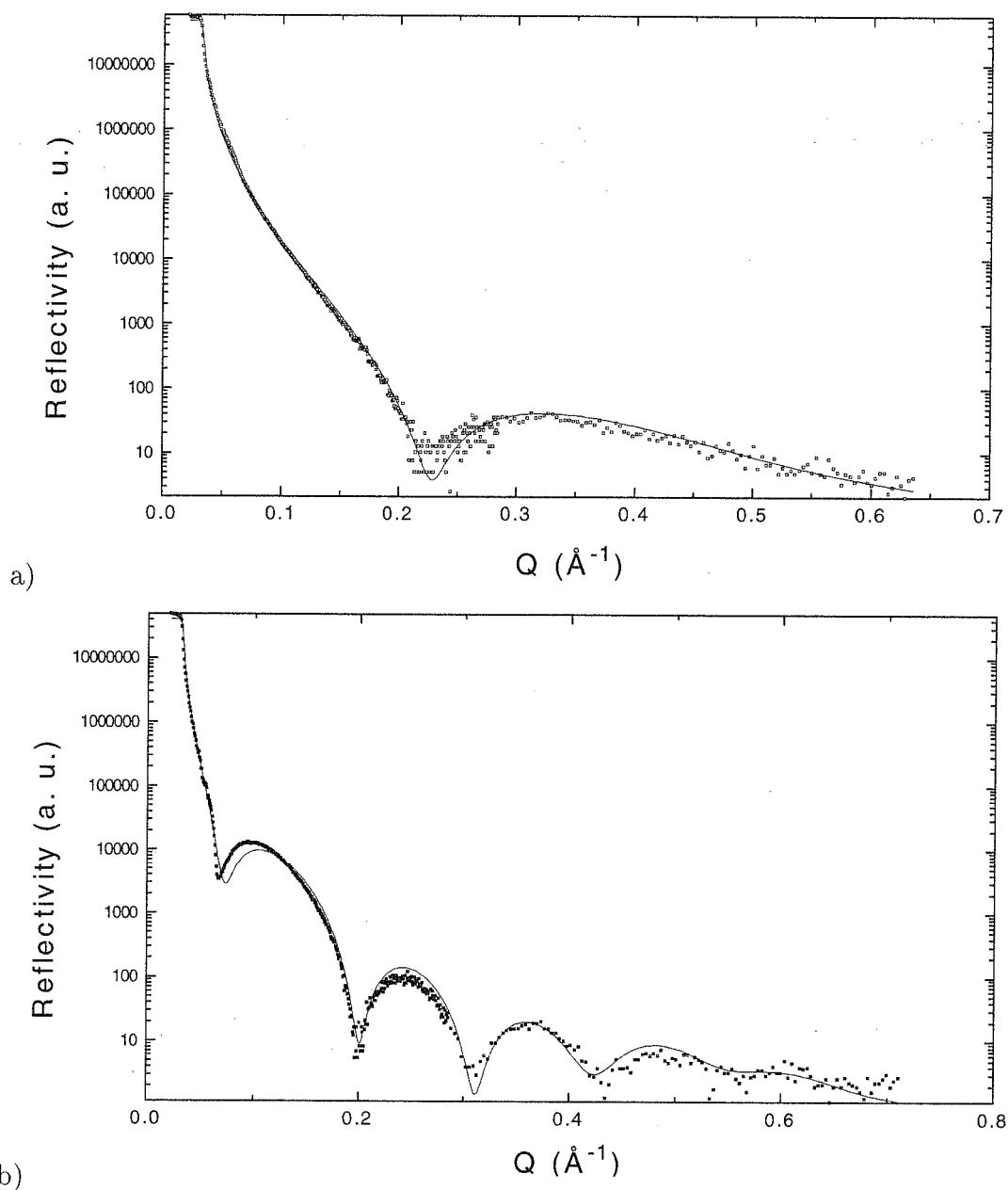


Fig. 5. — Reflectivity curves of the transferred a) monolayer and b) mono plus second interdigitated bilayer.

almost model independent from the Kiessig minima. If we subtract from the value obtained for the total multilayer thickness (50.3 \AA) the monolayer thickness (14.6 \AA), we obtain 36 \AA . This corresponds exactly to the value previously determined for the period of the bulk SmA phase [9]. We can thus assume that the structure of the top layers corresponds to that of the bulk.

4. Discussion and Conclusions

4.1. COMPARISON $5AB \leftrightarrow 10AB$. — We have shown that for $5AB$ equilibrium type isotherms can be measured between 5 and $60 \text{ }^\circ\text{C}$, whereas for $10AB$ this is possible only above $25 \text{ }^\circ\text{C}$.

This suggests that in the case of 10AB there is a crystalline phase involved and nucleation of this phase is time dependent. This is in accordance with the measured phase sequences for the bulk material. These results suggest that a condition for equilibrium isotherms is the involvement of fluid phases. For 5AB this is obviously the case even below room temperature. Therefore, compared to all others studied hitherto, this system is best suited for systematic and quantitative studies of layering transitions. For 10AB the distance between the disordering siloxane group and the ordering cyanobiphenyl smectogen is apparently too large to inhibit crystallization. On the other hand since the SmA phases of both compounds are equivalent [9], one can expect that similar layers are formed at the air/water interface when both systems are in the fluid smectic state.

4.2. MONOLAYER STRUCTURE. — According to the pressure/area isotherms the monolayer is in a single liquid phase for molecular areas between 60 \AA^2 and 46 \AA^2 . This is much larger than the cross section of the cyanobiphenyl group ($\cong 22 \text{ \AA}^2$). The lower value is close to the cross section of the siloxanes (43 \AA^2) [18]. This indicates that the latter determine the molecular area and that the cyanobiphenyl group is tilted. Since from BAM we know that the tilt is uniform we can estimate the tilt angle θ' from $\theta' = \arccos(22 \text{ \AA}^2/A)$. With the values of A given above we find that upon compression θ' is decreased from $\cong 69$ to 61 deg. This value is different from the 50 deg. derived above for the orientation of the molecule on solid support. The difference may be explained by a slight structural change during transfer or, more probable, by a cyanobiphenyl orientation more towards the surface compared to the residual molecule. Such an arrangement has previously been proposed for a similar system [19]. Altogether we may conclude that there is a uniform tilt of the molecule near 50 deg. and that this tilt angle is preserved quantitatively during transfer. We note that this tilt which is also present in the monolayer of 8CB, reduces the dipolar interaction between the cyano groups and therefore the electrostatic energy [20,21].

4.3. MULTILAYER STRUCTURE. — Because of its liquid-crystalline state, when collapsed, the monolayer does not crystallize on compression and undergoes a smectic like multilayer formation at points M_1 , M_2 and M_3 . The first sharp break in these isotherms (at M_1) occurs when the molecules in the monolayer have the closest possible packing allowed by the bulkier siloxane part with an area of about 43 \AA^2 [18]. To reveal the nature of the upper layers, it is interesting to form the ratios of M_1 by M_2 and M_3 . When these ratios are integers (2, 3, etc.) the successive transitions can be interpreted as an addition of one molecular layer on top of the first one at each step with the same internal structure within the successive layers. In the present case, however, these ratios are about 3.5 and 5.7. This means that the areas per molecule in the monolayer and in the multilayer differ considerably. The different parts of the molecules have different cross-sections. Therefore the molecules can form different internal structure for the monolayers and the multilayers on top due to the balance between intermolecular interaction and substrate effects, or/and the incommensurability of the layers. Hence, the physical meaning of the ratios is not always obvious.

In the present case, using simple geometrical considerations, one can understand quantitatively the values of 3.5 and 5.7 by assuming that the molecules in the monolayer are oriented with the cyano dipoles tilted with respect to the water surface. Those in the upper layers are overlapping with a certain degree of head to head association (τ) through their cyano dipoles as in the bulk smectic A_d mesophase [10].

The total area of the trough, occupied by N spread molecules in the monolayer at the transition point M_1 , is $\Sigma_1 = N A_{mo}$. With A_{mo} the area per molecule in the closed monolayer bound to water. At point M_2 , $2n_2$ molecules form a bilayer on top of the monolayer which

contains n_1 molecules (with, $2n_2 + n_1 = N$). The total area of the trough is decreased to $\Sigma_2 = n_1 A_{\text{mo}}$. We obtain also $\Sigma_2 \cong n_2 A_{\text{bi}}$, with $A_{\text{bi}} = 2V/d \cong \sigma_{\text{ar}}(2 - \tau)$ as average molecular area in the bilayer [10]; σ_{ar} is the area of the aromatic part ($\cong 22 \text{ \AA}^2$), V is the molar volume, and d is the smectic period. This leads to a ratio: $\Sigma_1/\Sigma_2 = 1 + 2A_{\text{mo}}/A_{\text{bi}}$. For the third layer, the same procedure gives: $\Sigma_1/\Sigma_3 = 1 + 4A_{\text{mo}}/A_{\text{bi}}$.

If we assume that the molecules in upper layers possess the same molecular area as in the bulk smectic A_d mesophase ($A_{\text{bi}} \cong 38 \text{ \AA}^2$) [9] and take the experimental value of $A_{\text{mo}} \cong 46 \text{ \AA}^2$ we find: $\Sigma_1/\Sigma_2 \cong 3.4$ and $\Sigma_1/\Sigma_3 \cong 5.8$. This is in agreement with the experimental data. We note that Σ_1/Σ_i does not explicitly depend on σ and τ but on A_{bi} , the molecular area in the multilayer. Hence the value derived does not depend on a model with monomers or dimers but, more abstractly, on the assumption $A_{\text{bi}} = 38 \text{ \AA}^2$. For $A_{\text{bi}} \cong \sigma_{\text{ar}}(2 - \tau)$ we used the value at 20°C , but notice that it can depend on external parameters like temperature or pressure. Yet we realize that both, Σ_1/Σ_2 and Σ_1/Σ_3 agree with the model, and that the value of A_{bi} is consistent with the structural model for the bulk compound. On the other hand it is obvious that the data contradict the formation of the upper layers as monolayers ($\tau = 0$) or bilayers ($\tau = 1$) with the same structure as the monolayer at the air/water interface. In this case we would obtain $\Sigma_1/\Sigma_2 = 2$ and $\Sigma_1/\Sigma_3 = 3$ or $\Sigma_1/\Sigma_2 = 3$ and $\Sigma_1/\Sigma_3 = 5$, clearly outside the error margin of the experimental data.

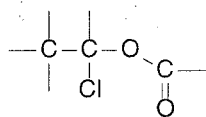
The conclusion from the isotherms that the upper layer structure corresponds to that of the bulk smectics is in accordance with the thickness measurement by X-ray reflectivity. Of course, for this we have to assume that the structures of the upper layers on water and on SiO_2 are identical. This assumption is reasonable, since in both cases the upper layers are not in immediate contact with the support.

Compared to other systems the present one also presents the advantage that the states involved in the layering transition correspond to thermodynamic equilibrium. E.g. for HOBACPC [2] the low molecular area ($\cong 17 \text{ \AA}^2$) at the onset of the transition indicates that there is not just a monolayer at the air/water interface. The upper layers are probably unpolar smectics, however, the conjecture from isotherms that they agree structurally with the lower layer is hard to believe. The present conclusions are in accordance with the case of the 8CB cyanobiphenyl compound [4] which presents a first order transition from a tilted monolayer to a monolayer plus an interdigitated bilayer similar to the bulk SmA [22]. In this case, using the available molar volume ($V_{8\text{CB}} \cong 495 \text{ \AA}^3$ [23]) and the smectic period ($d_{8\text{CB}} \cong 29 \text{ \AA}$ [24]), one can estimate the average molecular area of 8CB in the interdigitated smectic bilayer: $A_{\text{bi}} = 2V/d \cong 34 \text{ \AA}^2$. Consequently, the experimental value of $\Sigma_1/\Sigma_2 \cong 3.6$ obtained from the isotherm in reference [4] can be understood using the same model described above ($\Sigma_1/\Sigma_2 \cong 1 + 2 \times 42/34 \cong 3.5$).

4.4. THERMODYNAMICS OF THE MONO-MULTILAYER TRANSITION. — The transition from mono- to multilayer can be described as a first order phase transition with latent heat L and transition entropy $\Delta S = \frac{L}{T}$ using a two-dimensional Clausius-Clapeyron equation: $\frac{d\pi_c}{dT} = \frac{L}{T(A_2 - A_1)}$; with $\frac{d\pi_c}{dT} = -0.08 \frac{\text{mN}}{\text{m K}}$, $A_2 - A_1 = 35 \text{ \AA}^2/\text{molecule}$ we obtain for 300 K: $L = 5.0 \text{ kJ/mol}$. Since neither $\frac{d\pi_c}{dT}$ nor $A_2 - A_1$ strongly depend on temperature this also holds for L and thus we can easily calculate for the entropy $\Delta S = \frac{L}{T} = 17 \text{ J/mol K}$.

Interesting is also the value of the second step which is almost unaffected by the temperature $\frac{d\pi_2}{dT} \cong 0 \frac{\text{mN}}{\text{m K}}$ (Fig. 3a). This is in agreement with the fact that the upper interdigitated layers are similar and no enthalpy should be involved in the transition from one upper layer to another.

The values of L and ΔS are a factor of 3 larger than those derived for HOBACPC, but can be understood in a similar way. The entropy change in going from a polar to an unpolar ordering is maximally 2.9 J/mol K [2], and we therefore have to ascribe the main entropy change to a change in water ordering. The larger value can be understood due to the larger polarity



of the cyano group compared to the less hydrophilic moiety of HOBACPC.

On the other hand with the measured area change $A_2 - A_1 = 35 \text{ \AA}^2/\text{molec.}$ we can convert the latent heat L into a change in surface energy $\Delta E = \frac{L}{6 \times 10^{23} \left(\frac{\text{Molec.}}{\text{mol}} \right) \times 35 \left(\frac{\text{\AA}^2}{\text{Molec.}} \right)} =$

$24 \left(\frac{\text{mJ}}{\text{m}^2} \right)$. The major contribution to ΔE results from the removal of the surfactant from the air/water interface at $\pi_1 (\cong 15 \text{ mJ/m}^2)$. The additional interfacial energy of about 9 mJ/m^2 may be required to create the SmA/SmC interface. This seems a high value but may be not unreasonable since the energy corresponding to the difference in adhesion energy between parallel and perpendicular orientation for some mesogens is about 6 mJ/m^2 [1]. This large difference in the surface energy means that the orientation of the first layer cannot be modified by elastic deformation of the LC where the energy is at most 10^{-2} mJ/m^2 .

4.5. THICKNESS UNIFORMITY. — The present system displays a remarkable thickness uniformity (the upper layers do not spread out to form multilayers). This can be understood by two different ways:

- ◆ Nonuniform layer thickness requires energy to form domain boundaries. The boundary energy of a singular circular domain of radius R and height h is $E_b = \gamma 2\pi R h = 2V\gamma/R$ if we assume for the boundary surface, $2\pi R h$, the same interfacial energy as for the film/air interface ($\gamma \cong 20 \text{ mN/m}$). It scales like $1/R$ at constant volume V . For an average radius of $50 \text{ }\mu\text{m}$ and a height of 36 \AA (interdigitated bilayer thickness), the boundary energy of one domain can be estimated to $2.3 \times 10^{-14} \text{ J} \gg kT$. This will always smoothen the domain boundaries against thermal fluctuations. If a bilayer domain would spread to form, say, a smaller uniform domain containing two bilayers with a radius of $R/\sqrt{2}$, the line energy would increase by about 40%. This means that it is unfavorable to start the next layer before the first one is closed completely.
- ◆ The long-range v.d.W. contribution between the water surface and the film/air interface can be described by the van der Waals attraction E_i between two interfaces a distance d_i apart which scales like $E_i = \frac{A}{12\pi \times d_i^2}$. In this equation A is the difference of the Hamaker constants between water/air and between water/film/air. E_i contributes to the surface energy, and for the upper layers 50.4 \AA and 86.4 \AA apart from the water surface these contributions amount to $10 \times 10^{-6} \left(\frac{\text{\AA}}{\text{\AA}^2} \right)$ and $4 \times 10^{-6} \left(\frac{\text{\AA}}{\text{\AA}^2} \right)$, respectively. Even if we assume a very large Hamaker constant of about $40 \times 10^{-20} \text{ J}$ [25], the v.d.W. energy contributions to the second and the third steps can be estimated to only 0.44 and 0.16 mJ/m^2 . For a singular domain of radius $50 \text{ }\mu\text{m}$, these contributions correspond to $1.3 \times 10^{-12} \text{ J}$ and $3.5 \times 10^{-12} \text{ J}$. Since the Hamaker constant is not known and since we have assumed a probably too high value of A , it is hard to decide which of the two energies (line or v.d.W) is more relevant for the stability.

Concerning the surface pressure steps at M_i , the v.d.W. contribution is still too small. This suggests that other contributions (electrostatic, ...) are more relevant. This hypothesis is under investigation with SHG and surface potential measurements.

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