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Cylindrical growth of smectic A liquid crystals from the isotropic phase in some binary mixtures (*)

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Abstract. — In some binary mixtures of smectogenic and non-mesomorphic aliphatic compounds, the smectic A phase separates in the form of cylindrical structures. Our observations on some of these systems indicate that such structures are stabilised by a negative radial concentration gradient of the non-mesomorphic component. If the concentration of the non-mesomorphic component is allowed to increase in the isotropic phase, the cylindrical structures develop an undulation instability. It is argued that the concentration gradient leads to a spontaneous curvature in the smectic layers, which makes it necessary to include a term linear in curvature in the elastic energy density of such systems.

1. Introduction.

The smectic A liquid crystal phase is characterized by a periodic stacking of fluid layers of anisotropic molecules whose long axes are aligned normal to the layers on the average [1-3]. This phase can be easily identified under a polarising microscope by the focal conic texture, which is characteristic of such fluid layers. Many compounds exhibit the phase sequence Isotropic (I)-Nematic (N)-Smectic A (S_A) as the sample is cooled, while some others go over directly to the S_A phase from the isotropic liquid. Usually the S_A phase separates from the higher temperature phase in the form of batonnets, which are elongated structures consisting of focal conic domains [1].

We found sometime ago that in some binary mixtures of certain liquid crystals with aliphatic non-mesomorphic compounds the growth of the smectic A from the isotropic phase occurs in the form of long cylindrical structures. Indeed similar observations were made in early seventies by Meyer and Jones, but reported only recently [4] and more recently by Adamczyk [5]. Arora *et al.* [6] have found such structures in a single component system. In this paper, we describe our detailed observations on the growth of the cylindrical structure, which under certain conditions, develops an instability towards a beaded configuration. Our

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observations clearly indicate that concentration gradients lead to a spontaneous curvature of the layers and hence to these configurations. We present a simple model in which a linear term in curvature is included in the elastic energy density to qualitatively account for the observations.

2. Observations and discussion.

It is possible to suppress the nematic phase in compounds exhibiting I-N-S_A sequence by adding various kinds of non-mesomorphic impurities, like benzene or a long chain alcohol, etc. The phase diagram of the binary mixtures of octyloxycyanobiphenyl (8OCB) with dodecyl alcohol (DODA) is shown in figure 1. The N phase is suppressed for a molar concentration $x > 20$ % of the alcohol. Beyond this concentration, we get a fairly wide two phase region in which the isotropic and S_A phases coexist. At low concentrations of the alcohol, the smectic A liquid crystal separates from the isotropic phase in the form of batonnets, as usual (Fig. 2). For higher values of x, the growth pattern of the S_A phase changes. As the sample is cooled at ~ 0.1°/mn say, the smectic A appears initially in the form of a number of spherical droplets (Fig. 3a) which grow in size and after attaining a radius of ≃ 3-4 μm, start elongating into a cylindrical structure (Fig. 3b). They rapidly grow to lengths ≃ 500 μm or more at a temperature which is 2-3° below that at which they form, retaining a constant diameter. If the cooling is continued the cylinders suddenly collapse forming a compact drop which exhibits either focal conic defects or is homeotropically aligned (Fig. 3c). The elongated structures form in a wide variety of mixtures. For example in contact preparations of 8OCB and a variety of alkyl alcohols, we can see the formation of such structures all the way from ethyl alcohol to dodecyl alcohol. The longer alcohols give rise to longer filaments and the shorter alcohols give only a few short filaments. Even alkanes like

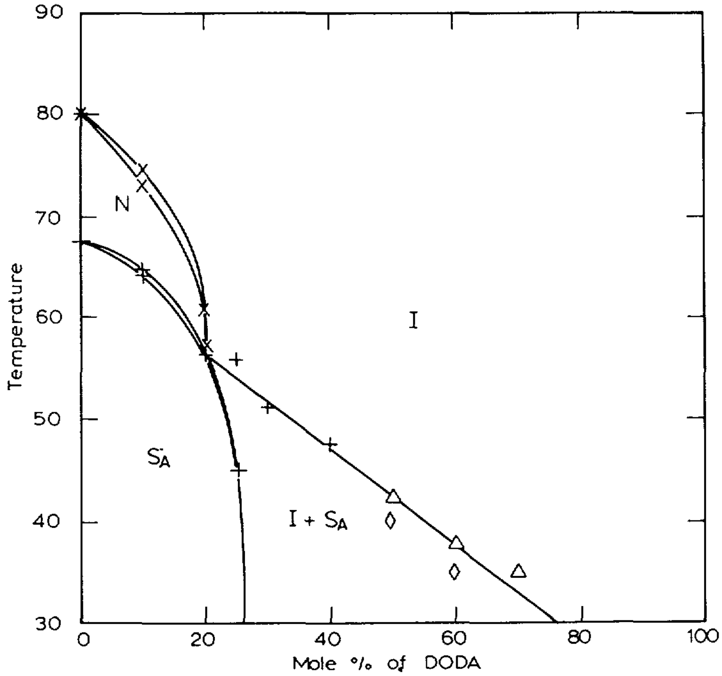


Fig. 1. — Phase diagram of mixtures of 8OCB and dodecyl alcohol.

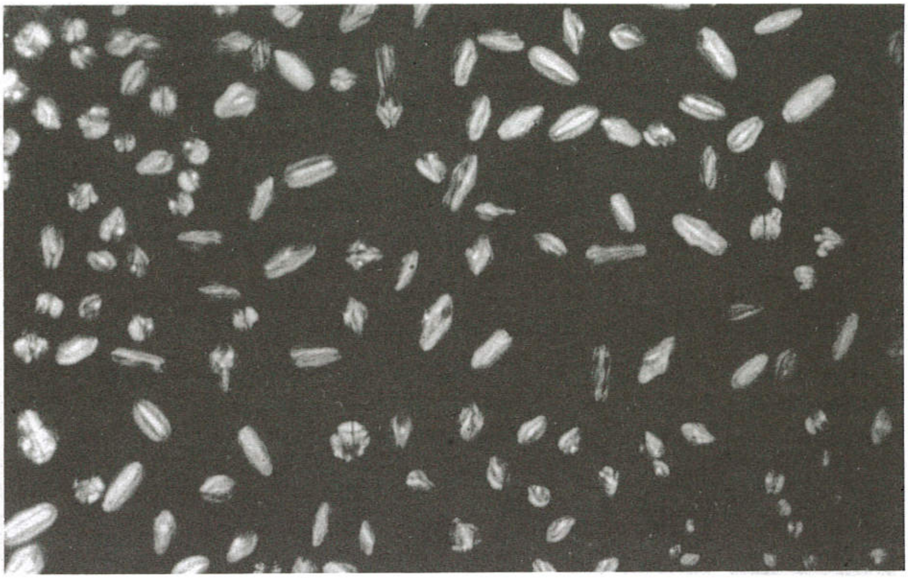


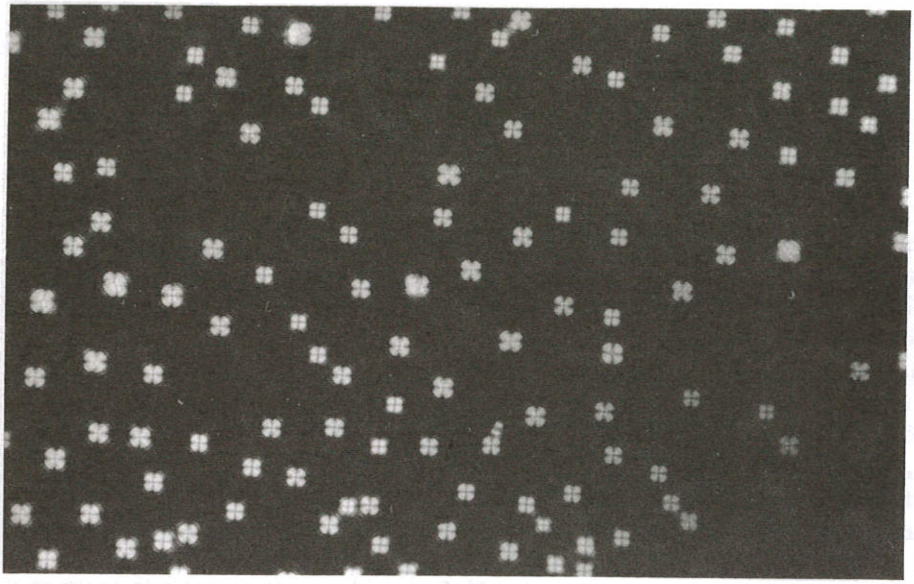
Fig. 2. — The S_A phase separating out from the isotropic phase in the form of batonnets in a sample of diethyl azoxy dicinnamate. Crossed polarisers (× 250).

decane or acids like decanoic acid give rise to similar structures with 8OCB, but not as efficiently as dodecyl alcohol. On the other hand, chemicals like benzene which also suppress the N phase of 8OCB do not give rise to the growth of such structures. In these cases, the separation of the S_A phase from the isotropic phase has been found to occur only in the form of batonnets.

The filamentary structure is found to occur in smectogens having many different chemical structures. For example, mixtures of dodecyl alcohol with diethylazoxydicinnamate also exhibited the filamentary growth, i.e., the polar nature of the mesogenic compound is unimportant. It is however curious that diethylazoxydibenzoate which differs from the cinnamate in that it does not have a CH=CH group at each end, does not form the filamentary structures. Pentylcyanoterphenyl exhibits only a nematic phase. When mixed with dodecyl alcohol it forms an induced smectic A phase which for a certain range of compositions directly goes over to the isotropic phase as the temperature is raised. Filamentary structures are formed in this system also. We have not found such a growth if the S_A phase separates from the nematic phase.

We might also note that these cylindrical structures are somewhat reminiscent of the myeline forms exhibited by lyotropic lamellar phases [7], though the elongation in the latter case appears to be much shorter. In the ideal smectic order which would not cost any elastic energy the equidistant layers lie flat on one another. Such a structure can be obtained for example by cooling the sample across the N-S_A transition from a homeotropically aligned sample if the glass plates are optically flat.

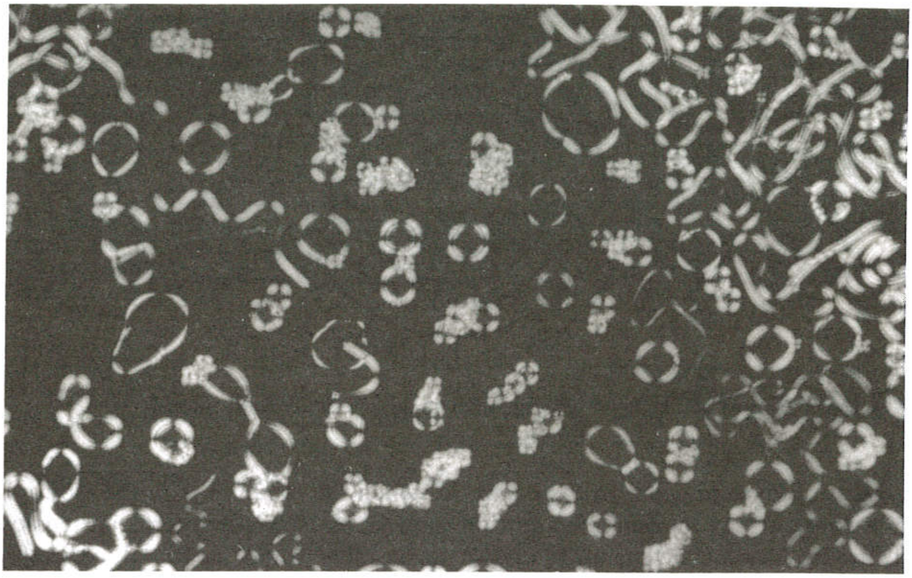
When we cool a binary mixture with alcohol concentration x with coexisting S_A and I phases to a temperature T_1, smectic A droplets with a composition x_1 which is very much richer in the smectogenic compound than x separate from the I phase (Fig. 4). In the I phase in the immediate vicinity of such a droplet the concentration of alcohol is higher than x and hence smectogenic nuclei cannot form in very close locations. Hence such droplets cannot



a)

b)

Fig. 3. — a) The S_A phase appearing from the isotropic phase in the form of tiny spherical droplets in a mixture of 8OCB and dodecyl alcohol in the molar ratio of 50 : 50 (hereafter referred to as x_{50}). Crossed polarisers (× 250). b) Rapid growth of the S_A cylinders as the sample shown in figure 3a is cooled. c) Collapse of the S_A cylinders shown in figure 3b into compact drops.



c)

Fig. 3 *(continued)*.

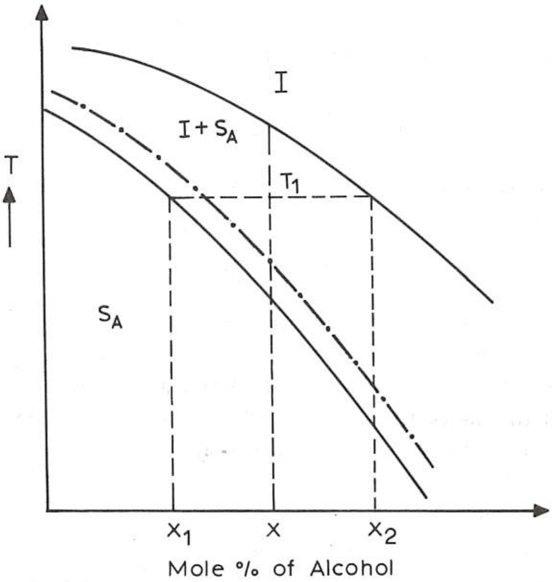


Fig. 4. — Schematic phase diagram of the experimental mixtures. The significance of the dotted line is explained in the text.

merge to form batonnets. As the temperature is lowered, the overall composition of the S_A phase can accommodate a higher percentage of alcohol than x_1.

The drops can be expected to have a spherical shape, in order to minimise the interfacial energy. The spherical shape is also compatible with the layer structure of the S_A phase (Fig. 5). This structure involves a point defect at the centre of the sphere. In practice, a core

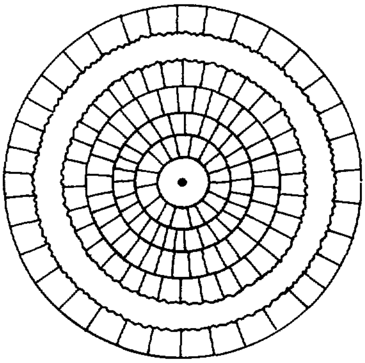


Fig. 5. — A cross-section of the layer arrangement in a spherical S_A droplet.

region can be expected to occur in the centre in which the medium is in the isotropic phase. We are not aware of any measurements of the smectic A-isotropic interfacial tension γ. The nematic-isotropic interfacial tension is known to be quite small, $\simeq 10^{-2}$ dyn/cm [8].

As we cool the sample, the spherical A domain can grow by adding an extra layer on top of the outermost layer. This process requires the nucleation of the next layer by the aggregation of a few molecules. However the nucleation costs energy as it exposes an extra interfacial area. If the nucleus of the extra layer is in the form of a circular region with radius « a » the additional interfacial area is $2\pi ad$, where d is the layer thickness, and the corresponding energy of the nucleus is $2\pi ad\gamma$. The layered smectic A phase has a lower Gibbs free energy at the given temperature than the isotropic phase. This gain in the energy ΔG is proportional to the volume of the *nucleus*, i.e.,

$$\Delta G = -\pi a^2 d(\delta g) \tag{1}$$

where δg is the difference in the free energy densities between the two phases. Therefore the net energy of the nucleus :

$$E_{\text{nucl}} = 2\pi ad\gamma - \pi a^2 d(\delta g) . \tag{2}$$

For a very small radius a, the first term predominates. As the energy is positive, the nucleus dissolves in the isotropic phase [9]. On the other hand, if $a > a_c = 2\gamma/\delta g$, the energy of nucleation becomes negative. There is a potential barrier at $a_c/2$ and if the nucleus has a radius $> a_c/2$ it grows to form a full layer to exploit the lowering of the free energy. An alternative way of increasing the size of the smectic A domain without nucleation of an additional layer is to absorb molecules through the outermost layer. If the spherical drop has to grow by this process, the isotropic core should also increase in size by an appropriate amount.

The absorption process can become quite efficient if the shape of the smectic domain itself changes, by elongating along some direction to become a spherocylinder (Fig. 6). It is clear that in this process the number of layers does *not* increase. This structure has got, apart from the two hemispherical caps a cylindrical section which has a line defect of strength + 1 at the centre.

If the molecules that are absorbed give rise to an elongation $\delta\ell$ the volume added is $\pi r^2 \delta\ell$, where r is the radius of the cylinder. Equating this with the volume of the « nucleus » of a new layer described above,

$$\delta\ell = \frac{a^2}{r^2} d . \tag{3}$$

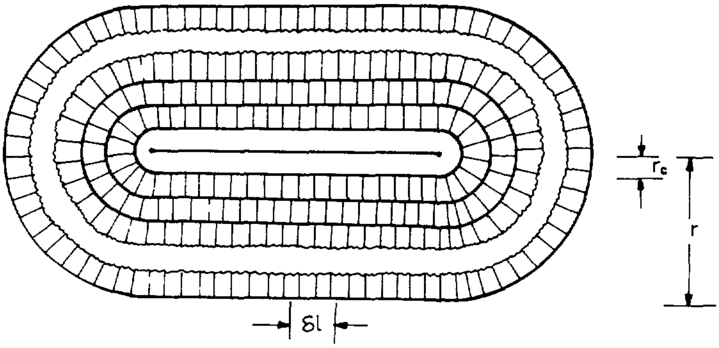


Fig. 6. — A cross-section of the layer arrangement in a cylindrical structure through its axis.

The extra surface area in the cylindrical growth is

$$2\pi r\,\delta\ell = \frac{2\pi a^2 d}{r} \tag{4}$$

This extra length also costs a curvature elastic energy [1] $\delta\ell\, K_{11}\, \pi \ln\frac{r}{r_c}$ where K_{11} is the splay elastic constant. Therefore ignoring the surface energy of the core at the centre of the cylinder, the total energy required to elongate the cylinder by $\delta\ell$ is given by

$$F_{\text{cyl}} = \frac{2\pi a^2 d\gamma}{r} + \frac{a^2}{r^2} d\, K_{11}\, \pi \ln\frac{r}{r_c} + \Delta G\,. \tag{5}$$

We can compare this with the corresponding « nucleation » energy of a new layer

$$F_{\text{nucl}} = 2\pi a d\gamma + \Delta G\,. \tag{6}$$

It is clear that for a given value of « a », $F_{\text{cyl}} < F_{\text{nucl}}$ for a sufficiently large value of r, as the logarithmic part increases only slowly with r. If for example, $a \simeq 0.2$ μm, $\gamma \simeq 10^{-2}$ dyn/cm, $K_{11} \simeq 10^{-6}$ dyn and $r_c \simeq 0.1$ μm, for $r \approx 0.5$ μm it is more favourable to elongate to a cylindrical structure rather than nucleate an extra layer which is large enough to grow into a full layer around the spherical object. In the experiment, we find that the radius of a typical cylinder is ≈ 3 μm.

The molecules absorbed by the outermost layers from the surrounding isotropic phase should reach the inner layers, all the way down to the isotropic core at the centre so that the whole structure can lengthen uniformly [4]. If the flux of molecules being absorbed at the outer layers is J_s and is a constant with time, the volume added per unit time (ignoring the hemispherical caps) is

$$2\pi r \ell v_0 J_s = \pi r^2 \frac{\mathrm{d}\ell}{\mathrm{d}t} \tag{7}$$

where v_0 is the volume of one molecule

or

$$\ell = \ell_0 \exp\left[\frac{2 v_0}{r} J_s t\right] \tag{8}$$

i.e., the length increases exponentially with time. This accounts for the rather rapid increase in the length of the filamentary structure. (It is reminiscent of the initial growth of whisker crystals though the detailed mechanisms are different [9].) The radial motion of the molecules from the outer layer to the interior is through the process of permeation, as we have a layering order in this direction, i.e., the molecules have a jump like diffusion from layer to layer. The chemical potential difference between the outer and inner layers drives this flux of molecules. In a simple minded approximation, the permeation time to the interior

$$\tau \simeq r^2/D_{\parallel} \tag{9}$$

where the diffusion constant $D_{\parallel} \simeq \lambda_p B \simeq 10^{-5}$ cm^2/s, where B is the compression modulus of the layers and λ_p the permeation coefficient [1]. For $r \simeq 4$ μm, we get $\tau \simeq 0.02$ s. We should allow enough time for the molecules to reach the core through the permeative diffusion process. Experimentally, a cooling rate of 0.1°/mn produces a high elongation of the filament. On the other hand, a cooling rate of 0.6°/mn is too fast and the elongation is restricted, for the same temperature difference.

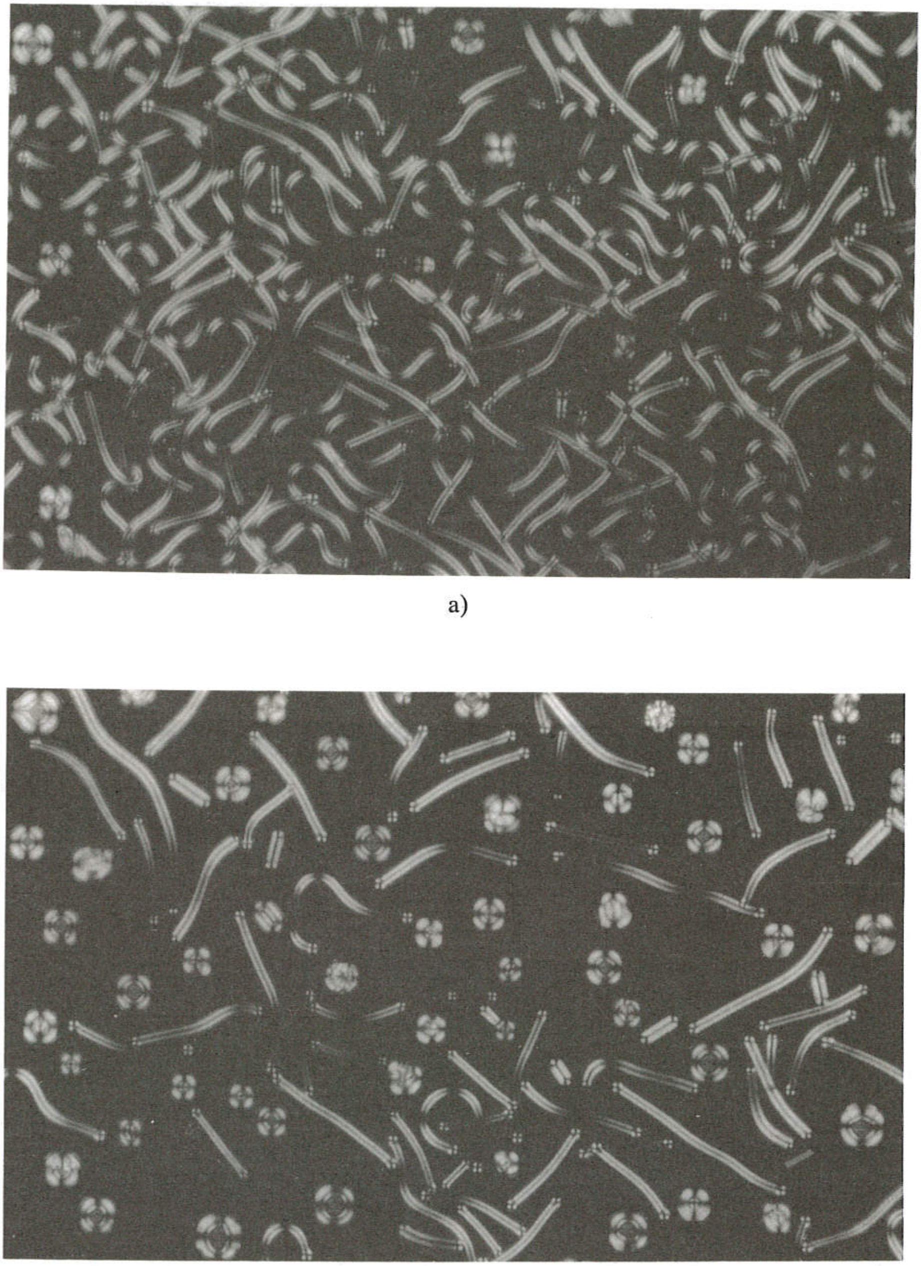
If the cooling is stopped abruptly after sometime, the subsequent evolution of the cylinder depends on its diameter. The thinner cylinders (see Figs. 7a and 7b) with a radius ≤ 3 μm which would have grown to a considerable length in view of the $1/r$ factor in the exponential of equation (8) would slowly shrink in length over a period of ~ 1/2 an hour or so. The diameter does not change during this process and the molecules are desorbed through the outer layers in a process which is the reverse of the one described earlier. Indeed even spherical droplets which had not elongated also disappear during this time.

On the other hand, the thicker and hence shorter cylinders with a radius > 4.5 μm have a different evolution. Typically after about 10 mn of maintaining them at a constant temperature, they develop an undulation instability (Figs. 8a and 8b) in which the cylinder gets a beaded appearance. After this instability develops, the material in successive beads merge to form a large compact structure in about a minute.

Simultaneously with the above processes, we could see the growth of flat homeotropic layers from some parts of both of the glass plates confining the sample. Obviously the lowest energy state would correspond to the flat layers. If we prepare the sample between glass plates having corrugated surfaces by an appropriate grinding technique, the above mentioned processes of shrinkage of the long and thin cylinders and the undulation instability of the short and thick cylinders can be delayed by several hours. Eventually one could see the growth of layers with focal conic defects from such ground surfaces (Fig. 9).

In the samples taken between smooth glass plates, if the cooling is resumed after waiting for about 10 mn, even the thin long cylinders develop the undulation instability. But in this case, the undulating structures very quickly collapse to compact units.

The above observations can be understood if we assume that at any given temperature the equilibrium concentration of alcohol in the layered structure *increases* with the curvature of the layers, i.e., $x = x(r)$ in the cylindrical and spherical drops. An increase in the alcohol concentration would reduce the S_A-I transition-point. At the given temperature, the orientational order parameter and hence the curvature elastic constant would then be reduced, bringing down the elastic energy associated with the curvature. Schematically, the boundary between the smectic A + isotropic coexistence region and the smectic A phase no longer appears to be a single line but is spread out over a range of concentrations. This range is shown in figure 4 to lie between the dotted line (corresponding to strongly curved layers) and the lower full line (corresponding to flat layers). In the cylinders and spheres the concentration $x(r)$ decreases with r, i.e., there is a negative radial concentration gradient of the alcohol molecules. The concentration profile depends on a dynamic balance between the flow of alcohol molecules towards a region of larger curvature to reduce the elastic energy and the outflow due to diffusion. We will not develop this approach in the present paper. We note

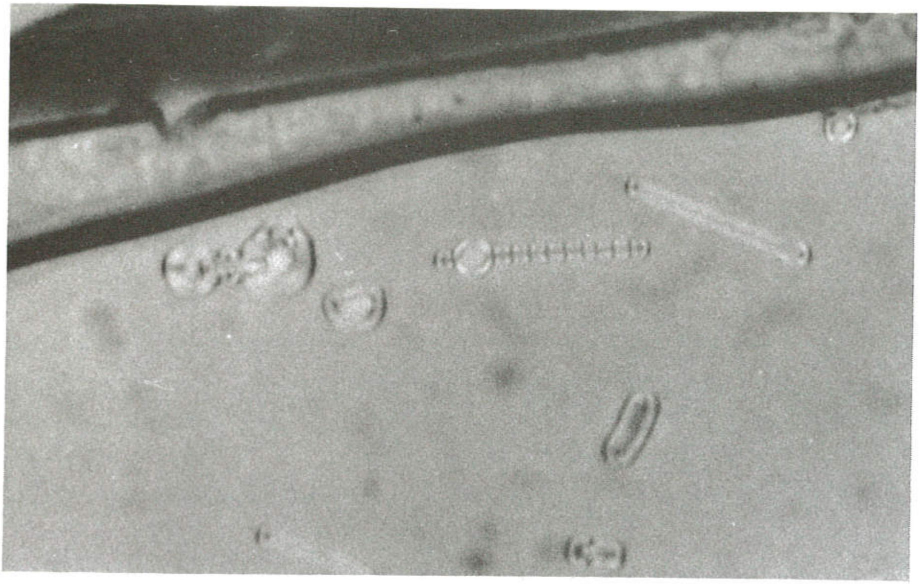


a)

b)

Fig. 7. — a) S_A cylinders forming in a sample of x_{50}. Crossed polarisers (× 250). b) Same sample as in figure 7a, photograph taken 10 mn after the cooling was stopped. Note that the cylinders have shrunk in length.

that in principle a concentration gradient can lead to a spontaneous curvature of the layer. We shall incorporate this effect in a very simple phenomenological model by assuming that the elastic energy density has a term *linearly* dependent on the curvature. If the corresponding



a)

b)

Fig. 8. — a) S_A cylinders formed in x_{50}. Photograph taken 10 mn after cooling was stopped. One thick cylinder has undergone the undulation instability. Polariser axis parallel to horizontal edge of the photograph, no analyser (× 100). b) Same sample as in figure 8a after another 5 s. The second cylinder has also undulated. Note that in the first structure, one of the *beads* has been absorbed into the big spherical unit. Polarizer axis perpendicular to horizontal edge of the photograph. No analyser (× 100).

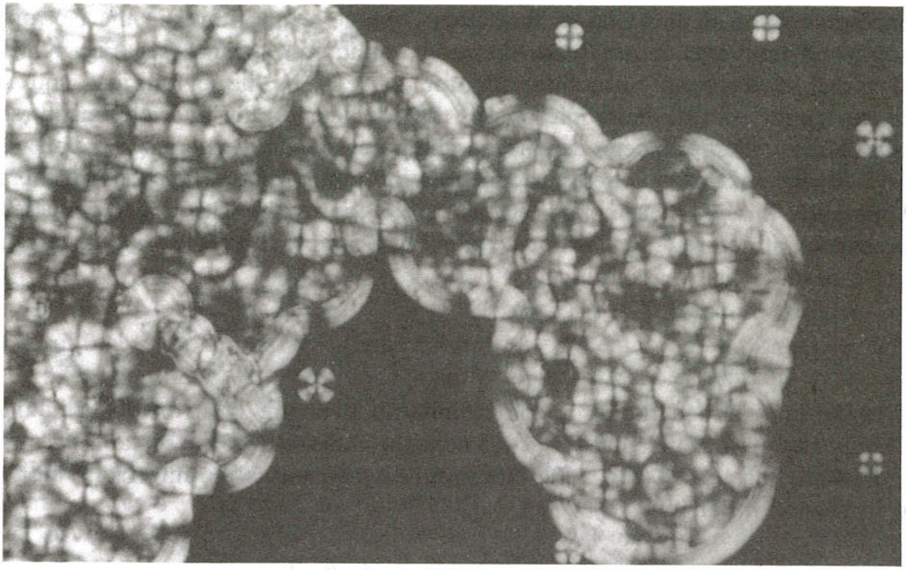


Fig. 9. — Growth of large S_A regions developing in the I phase in a sample of x_{50} taken between ground glass plates.

elastic constant is denoted by K_1, the total energy of a cylindrical structure is given by

$$E_{\text{cyl}} = 2\,\pi \ell \left[K_1 (r - r_c) + \frac{K_{11}}{2} \ln \frac{r}{r_c} + \gamma (r + r_c) \right] \tag{10}$$

where ℓ is the length and r the radius of the cylinder and r_c that of the core. We have ignored for simplicity the dependence of K_{11} and possibly of K_1 on r. If this cylinder collapses to form a spherical structure with a radius r_s and a corresponding core with radius r_{s_c}, the energy is given by

$$E_{\text{sph}} = 4\,\pi\,[K_1 (r_s^2 - r_{s_c}^2) + 2\,K_{11} (r_s - r_{s_c}) + \gamma (r_s^2 + r_{s_c}^2)]\,. \tag{11}$$

In the last equation, we have ignored a term depending on the Gaussian curvature. Assuming that $K_{11} \simeq 10^{-6}$ dyn, and $\gamma = 10^{-2}$ dyn/cm and $\ell \simeq 100$ μm, the cylinder will have a lower energy than the sphere if $K_1 < -0.02$ dyn/cm. (The numerical value of K_1 needed to stabilise the cylindrical structure is not very high. If the spontaneous curvature were to arise due to a shape asymmetry of the molecules, $K_1 \sim K_B T/(\text{mol. area}) \sim 1$ dyn/cm.) The negative radial concentration gradient of alcohol $(\mathrm{d}x/\mathrm{d}r)$ apparently gives rise to the negative value of K_1.

The aliphatic alcohols can be expected to preferentially lie closer to the aliphatic end chains of the smectogenic molecules in the layers, rather than near the aromatic cores. We may recall here that the cylindrical structures are found if the smectogen is diethyl azoxydicinnamate but not when it is diethylazoxydibenzoate which has a shorter end group.

As we noted earlier, in a sample taken between two *flat* glass plates flat smectic layers slowly grow on the glass plates. Further, if a glass rod of ~ 10 μm diameter is inserted inside the axis of a capillary tube with an inner diameter of ~ 200 μm, the smectic layers grow only on the inside wall of the capillary rather than on the glass rod. The flat layers would have a lower concentration of alcohol and as they grow, the concentration x in the isotropic phase increases beyond the value required for thermodynamic equilibrium (see Fig. 4). There are now two possible ways of correcting the imbalance : (1) the cylindrical and spherical structures can dissolve in the isotropic phase, thus decreasing the overall concentration x in the latter. This is what happens when the diameter of the cylinder is relatively small ($r < 3$ μm). (2) The excess alcohol can penetrate the cylindrical structure from the isotropic phase. Apparently this is what happens in the case of cylinders with larger diameter, giving rise to the beaded structure (Fig. 8). For developing a simple model for this instability of the cylinder, we describe it by assuming [7]

$$r = r_{\mathrm{u}} + \varepsilon \sin \frac{2\pi}{P} z \tag{12}$$

where r_{u} is the undisturbed radius in the cylindrical structure lying between r_{c} and r. The amplitude ε is assumed to be small ($\varepsilon \ll r_{\mathrm{u}}$) near the threshold of the instability and P is the wavelength of the instability (Fig. 10). The instability increases the interfacial area which is given up to second order in ε, by

$$A = 2\pi P \,(r_{\mathrm{c}} + r)\left(1 + \frac{\varepsilon^2 \pi^2}{P^2}\right) . \tag{13}$$

The free energy of the undulated structure per unit length is given by

$$\begin{aligned} E_{\mathrm{und}} = {} & 2\pi K_1 (r - r_{\mathrm{c}})\left(1 - 2\frac{\varepsilon^2 \pi^2}{P^2}\right) + \\ & + \pi K_{11}\left[\ln \frac{r}{r_{\mathrm{c}}}\left(1 - 2\frac{\varepsilon^2 \pi^2}{P^2}\right) + \frac{\varepsilon^2}{4}(r^2 - r_{\mathrm{c}}^2)\left(\frac{1}{r^2 r_{\mathrm{c}}^2} + \left(\frac{2\pi}{P}\right)^4\right)\right] \\ & + 2\pi\gamma (r + r_{\mathrm{c}})\left(1 + \frac{\varepsilon^2 \pi^2}{P^2}\right) . \end{aligned} \tag{14}$$

The undulations will grow if $\partial E_{\mathrm{und}}/\partial \varepsilon^2 < 0$. The threshold condition is $\partial E_{\mathrm{und}}/\partial \varepsilon^2 = 0$. The optimum value of the pitch can be calculated using the condition $\partial E_{\mathrm{und}}/\partial(1/P^2) = 0$. At the threshold

$$P = 2\pi \sqrt{r r_{\mathrm{c}}} . \tag{15}$$

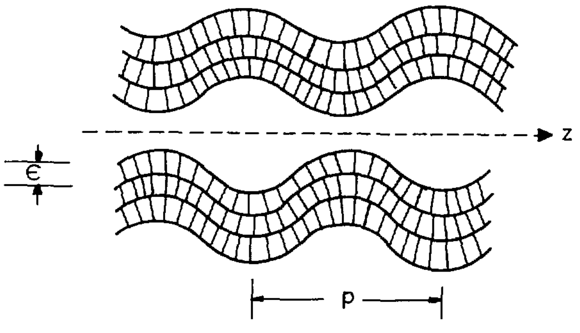


Fig. 10. — Schematic drawing of the undulation instability of the layers in a cylinder of S_A.

If $r \simeq 4\ \mu\mathrm{m}$ and $r_c \simeq 0.5\ \mu\mathrm{m}$, we get $P \simeq 8.5\ \mu\mathrm{m}$ which is $\simeq 2r$, as has been found experimentally. It is always possible to get $\partial E_{\mathrm{und}}/\partial \varepsilon^2 < 0$ if we assume an appropriate positive value of K_1, of the order of 0.017. Following our earlier discussion, this sign of K_1 implies a positive sign of the concentration gradient $\mathrm{d}x/\mathrm{d}r$. This becomes possible if the outer layers of the cylinder absorb the excess alcohol from the isotropic liquid. However as we noted earlier, only cylinders with a relatively large radius undergo this transition sometime after the decrease in temperature is halted. Indeed the dependence of $\partial E_{\mathrm{und}}/\partial \varepsilon^2$ on r is somewhat sensitive to the assumed values of r_c and the other physical parameters. However, assuming very reasonable values for these parameters, we can get the result that *$\partial E_{\mathrm{und}}/\partial \varepsilon^2 < 0$ for a limited range of values of r (Fig. 11). This could provide a possible* explanation of our observations. The unstable range of r is enlarged on increasing the value of K_1 (Fig. 11). The fact that even the thinner cylinders would develop the undulation instability if the sample is again cooled after maintaining the temperature for about 10 mn (Figs. 12a and 12b) indicates that at the lower temperature, the smectic A cylinders which can have a higher concentration of alcohol absorb a large enough number of alcohol molecules to attain the required value of K_1. However, as we noted earlier, a positive value of K_1 cannot stabilise the cylindrical structure itself against a collapse to a spherical one. Indeed the thinner cylinders collapse immediately after the undulation instability sets in. The thicker cylinders with undulation instability also collapse, though somewhat more slowly.

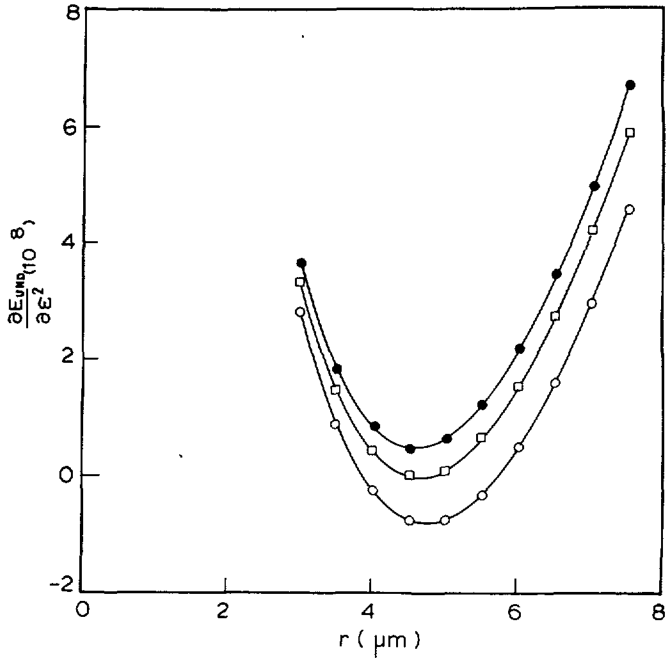
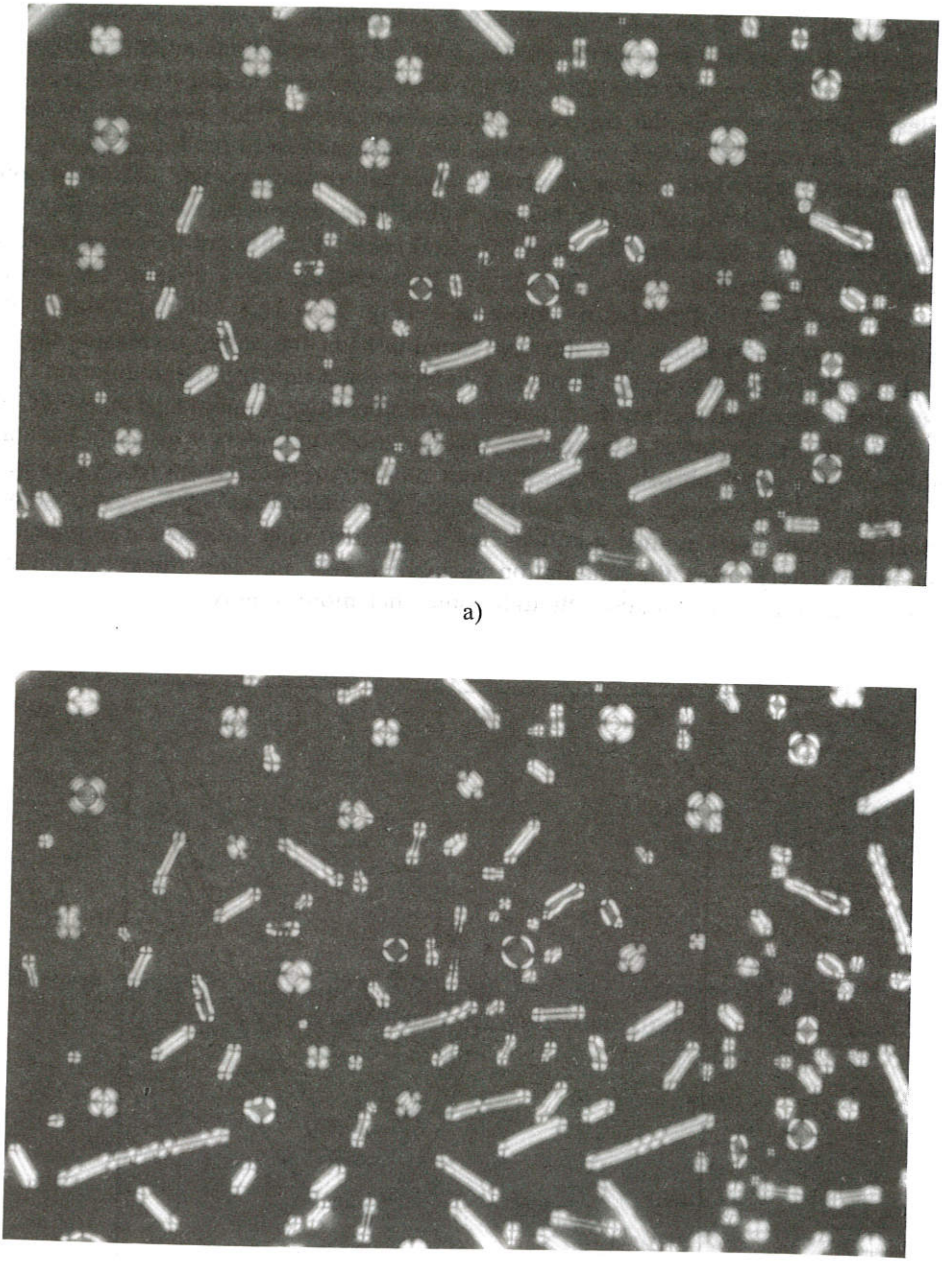


Fig. 11. — Plot of $\partial E_{\mathrm{und}}/\partial \varepsilon^2$ *vs.* r for K_1 equal to 0.01733 (●), 0.01734 (□) and 0.01736 (○).

It would be very useful to be able to measure the actual concentration profile in the cylindrical structure as a function of time to check the validity of the above argument. We have not been able to make such measurements. However we thought it worthwhile to monitor the path difference of the thicker cylinders as a function of time after cooling is halted



a)

b)

Fig. 12. — a) S_A cylinders formed in a sample of x_{50}. Photograph taken 15 mn after cooling was stopped. Crossed polarisers (× 250). b) Same sample as in figure 12a. Photograph taken as soon as cooling is resumed. Note that undulations develop in many cylinders. Crossed polarisers (× 250).

at some temperature. Referring to figure 13, we make the reasonable assumption that a ray of light traversing the cylinder vertically does not suffer any strong refraction effects at the isotropic-smectic interface if the ray is not far from the centre of the cylinder (i.e., a is

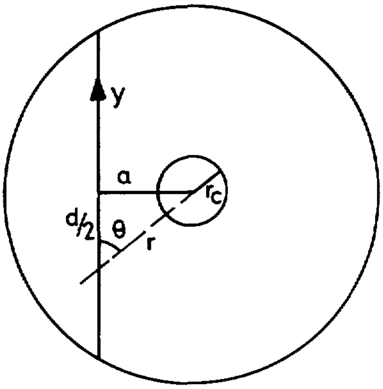


Fig. 13. — Cross-section of the cylinder on which light is incident in a vertical direction.

$\leqslant r/4$). The effective extraordinary index depends on the angle θ made by the local director with the radius vector (Fig. 13) :

$$n_{\text{eff}} = \frac{n_o\,n_e}{\sqrt{n_e^2\cos^2\theta + n_o^2\sin^2\theta}} \simeq n_o\left(1 + \frac{\eta}{2}\sin^2\theta\right) \tag{16}$$

where $\eta = \dfrac{n_e^2 - n_o^2}{n_e^2} \simeq 0.12$ if $n_e = 1.6$ and $n_o = 1.5$ for the pure smectogen.

As the concentration x depends on the radial distance, it is clear that η is not a constant.

The path difference between the extraordinary and ordinary rays along the path shown in figure 13 is given by

$$\begin{aligned} \Delta\ell(a) &= 2\int_0^{d/2} \Delta n_{\text{eff}}\,\mathrm{d}y \\ &\simeq 2\,n_o\int_0^{d/2}\left\{\frac{\eta(r)}{2}\right\}\sin^2\theta\,\mathrm{d}y \\ &\simeq n_o\int_0^{d/2}\left\{\eta_0 + r\frac{\mathrm{d}\eta}{\mathrm{d}r}\right\}\sin^2\theta\,\mathrm{d}y \end{aligned} \tag{17}$$

where we have assumed that n_o does not vary much with the concentration. For the sake of simplicity, we assume that $\mathrm{d}\eta/\mathrm{d}r$ is a constant. If $\mathrm{d}x/\mathrm{d}r$ is negative, $\mathrm{d}\eta/\mathrm{d}r$ should be positive, since the alcohol molecules can be expected to have a much lower optical anisotropy than the smectogenic molecules. It can be easily shown that

$$\Delta\ell(a) = n_o\,a\left[\eta_0[\pi/2 - \sin^{-1}(a/r)] - (\mathrm{d}\eta/\mathrm{d}r)\,a\ln\tan\frac{1}{2}(\sin^{-1}a/r)\right]. \tag{18}$$

If the sample is kept between crossed polarizers such that the axis of the cylinder makes an angle of 45° with them, the transmitted intensity is given by

$$I(a) = \frac{1}{2}\left[1 - \cos\left(\frac{2\,\pi\,\Delta\ell(a)}{\lambda}\right)\right]. \tag{19}$$

With $n_0 = 1.5$, $\eta \simeq 0.12$ and $d\eta/dr \simeq 0.0007/\mu m$, calculations show that the transmitted intensity has a maximum near $a \simeq 1.35$ μm (Fig. 14). If the concentration gradient and hence the value of K_1 changes with time, we can expect $d\eta/dr$ also to change. Indeed changing $d\eta/dr$ from $+0.0007/\mu m$ to $-0.0007/\mu m$, the calculations show that the intensity peak should shift from $a = 1.35$ μm to $a = 1.4$ μm, i.e., the separation between the maxima should enlarge by about 0.1 μm. The alcohol molecules are likely to have a very low value of $(n_e - n_0)$ in the liquid crystal matrix. If we assume that n_e of the alcohol is $= 1.52$ and $n_0 \simeq 1.50$, we get $\eta_{alc} \simeq 0.026$. Further assuming that $\eta_{mixt} = (1 - x)\, \eta_{lc} + x\eta_{alc}$, where the value corresponding to the pure smectogen $\eta_{lc} = 0.12$ it is clear that

$$\frac{d\eta_{mixt}}{dr} = (\eta_{alc} - \eta_{lc}) \frac{dx}{dr} \tag{20}$$

and $d\eta/dr \simeq 0.0007$ would correspond to $dx/dr \simeq 0.007/\mu m$, i.e., 0.7 %/μm which is not a very large value.

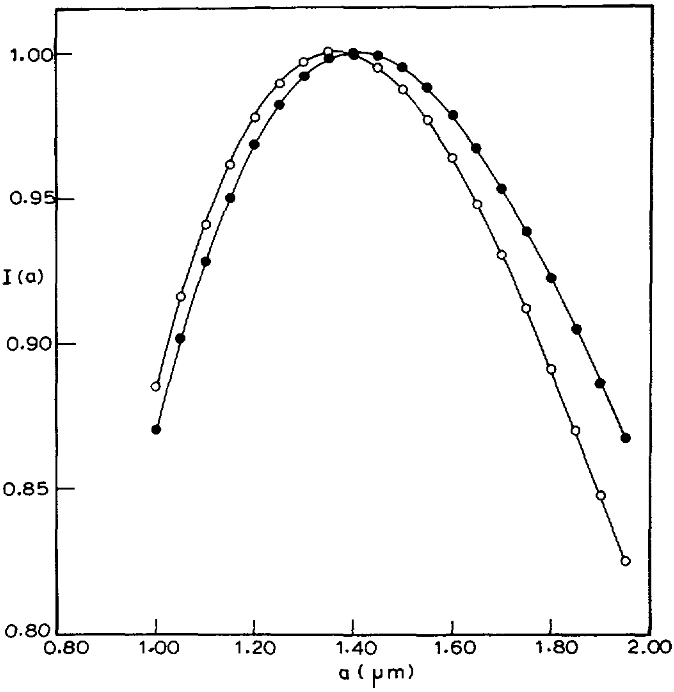


Fig. 14. — Calculated variation of the transmitted intensity as a function of « a » for a cylindrical structure, set at 45° between crossed polarisers : $d\eta/dr = 0.0007$ (○) and -0.0007 (●).

A cylinder of a relatively large diameter ($r \simeq 4.5$ μm) was oriented between crossed polarizers under the microscope such that the cylinder axis was at 45° to the polarizer. It was illuminated with an expanded beam from a 1 mW Helium-Neon laser. The fringes due to the interference of polarized light could be clearly seen using a CCD camera and a video monitor. The CCD camera was placed at such a distance from the output end of the microscope that the separation between successive pixels was $\simeq 0.3$ μm. The intensity profile of the interference pattern was caught by a frame grabber (Model DT2851) every 30 ms and the profile was averaged over 1 s. The averaged profile immediately after the cooling was stopped and after a waiting time of about 5 mn were compared (Fig. 15). In several independent

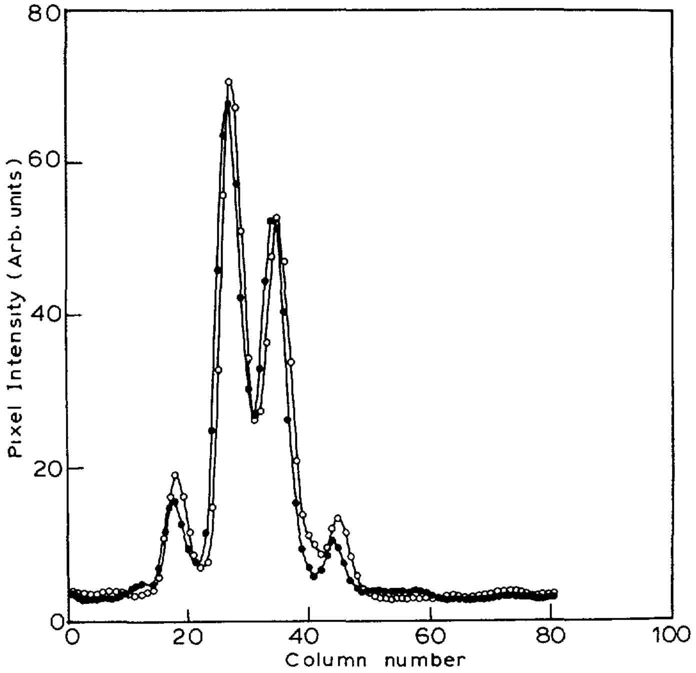


Fig. 15. — Experimental intensity profiles recorded by a CCD camera and averaged over 30 scans by a frame grabber. (●) Corresponds to average value obtained as soon as the cooling is stopped. (○) Corresponds to average value obtained after waiting at the same temperature for 5 mn.

samples, it was noted that the separation between the intensity maxima expanded by ~ 0.3 μm after such a waiting period. The cylinder usually underwent the undulation instability within a couple of minutes after the second run was taken. It is clear that the concentration profile is changing in the correct direction over the period of waiting, though we must add that the observation does not prove that dx/dr has actually changed sign.

We recall that if the temperature is steadily decreased at the rate of ~ 0.1°/mn, the cylinder with $r \simeq 3$ μm can grow to a length of ~ 500 μm and then suddenly collapse to a compact unit. As we cool the system steadily the smectic phase can accommodate an increasingly larger percentage of alcohol (Fig. 4). As the percentage of absorbed alcohol molecules steadily increases, the negative value of K_1 can be expected to become smaller and at some stage the cylindrical structure is no longer stable with reference to the spherical one (see Eqs. (10) and (11)).

In conclusion, our observations on the binary system 8OCB + dodecyl alcohol have shown that cylindrical structures can be stabilised relative to the spherical ones in such systems. The observations also clearly indicate that the equilibrium concentration of alcohol in the smectic A phase increases with the curvature of the layers.

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