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Growth patterns of smectic A liquid crystals

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Abstract

We report observations on the growth patterns of smectic A liquid crystals from the nematic phase in binary mixtures which exhibit an induced smectic phase. In cells prepared with 'homeotropic' boundary conditions there is a clear indication of a microphase separation which leads to nucleation of the smectic layers in the centre of the cell, and formation of single focal conic domains. The domains attract each other to form chains which is ascribed to flexoelectric polarization. A high-frequency AC field produces a corrugation of the interface, the spatial period of which decreases rapidly as the field strength is increased. Dust particle motion around the domains indicates that there may be electrohydrodynamic motion in the nematic liquid crystal surrounding the smectic domains.

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1. Introduction

Liquid crystals are systems which exhibit strong anisotropy in physical properties and yet have a certain measure of fluidity. The simplest type of liquid crystal is the nematic (N) one, which is characterised by a long-range orientational order without any translational order. The long axes of the molecules are aligned approximately parallel to one another. An apolar vector $\boldsymbol{n}$ called the director defines the average direction of orientation of the long axes. The smectic A (S_A) liquid crystal has a periodic stacking of liquid layers. In each layer the molecules on the average are oriented parallel to the layer normal.

The curvature deformations of a nematic can be described by the distortion free energy density [1]

$$F^N = \tfrac{1}{2}K_{11}(\operatorname{div}\boldsymbol{n})^2 + \tfrac{1}{2}K_{22}(\boldsymbol{n}\cdot\operatorname{curl}\boldsymbol{n})^2 + \tfrac{1}{2}K_{33}(\boldsymbol{n}\times\operatorname{curl}\boldsymbol{n})^2, \qquad (1)$$

where K_{11}, K_{22} and K_{33} are the elastic constants corresponding to splay, twist and bend respectively. The free energy density associated with the bulk elastic distortions of smectic A is of the form

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$$F^{\mathrm{A}} = \tfrac{1}{2}K\left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2}\right)^2 + \tfrac{1}{2}B\left(\frac{\partial u}{\partial z}\right)^2 , \qquad (2)$$

where u is the displacement of the layer from its equilibrium position. The first term is associated with the curvature elastic constant for bending of the layers with $K(=K_{\|}) \sim 10^{-6}$ CGS units. The second term describes the energy associated with layer dilation with $B \sim 10^8$ CGS units. Because of the large difference between K and B, we can assume that the layers remain equidistant but can be curved. Such an arrangement leads to the well known focal conic defects [2].

There have been several studies [2–8] on the growth patterns of smectic liquid crystals from the isotropic phase (I) which show that the shape of the smectic A droplet depends on the interfacial tension anisotropy $\Delta\gamma = \gamma_{11} - \gamma_{\perp}$, where the subscripts indicate directions parallel and perpendicular to the layer normal. Usually in pure compounds $\Delta\gamma$ is positive as the interfacial tension along the 'liquid' smectic layers can be expected to be relatively small. In such cases, smectic A droplets which separate from the isotropic phase have an ellipsoidal shape with flat layers which are perpendicular to the long axis of the ellipse. But in such a structure the layers are not perpendicular to the interface everywhere. The latter condition can be satisfied by a suitable bending of the layers, resulting in a focal conic domain. For a drop with a size $L > L_o \sim K/(\bar{\gamma} - \gamma_{\perp}) \sim K/\Delta\gamma$, the drop with the focal conic domain has a lower energy than the one with flat layers [3]. Recent studies on a pure long chain compound [4] and special types of binary mixtures [5–8] with appropriate compositions have shown that in these cases the $\mathrm{S_A}$ phase separates from the isotropic phase as long cylindrical structures with layers parallel to the interface. This implies that $\Delta\gamma$ is negative in these cases. In some cases the interfacial tension anisotropy is found to vary as a function of temperature giving rise to a rich class of structures.

In this paper we describe our experimental observations on the growth of the smectic A liquid crystals from the nematic phase in a binary mixture. The interfacial tension anisotropy in this case is positive. Different types of structures are found to develop, depending on the alignment imposed on the nematic by an appropriate treatment of the bounding glass plates. The effect of an electric field on the structure of $\mathrm{S_A}$ droplets has also been investigated.

2. Experimental

The compounds used in our studies are pentyl cyano terphenyl ($\mathrm{H_{11}C_5\text{-}C_6H_4\text{-}C_6H_4\text{-}C_6H_4\text{-}CN}$ or 5CT) with the phase sequence (on cooling) I-238.5°C-N and 4-biphenyl 4″-n-decyloxybenzoate ($\mathrm{H_{21}C_{10}\text{-}C_6H_4\text{-}COO\text{-}C_6H_4\text{-}C_6H_5}$ or BO10) with the phase sequence I-127°C-N-106°C-$\mathrm{S_A}$. The latter compound was synthesised in our chemistry laboratory [9].

Initially we prepared various binary mixtures and studied the phase transitions using a polarising microscope in conjunction with a Mettler hot stage. Fig. 1 shows the

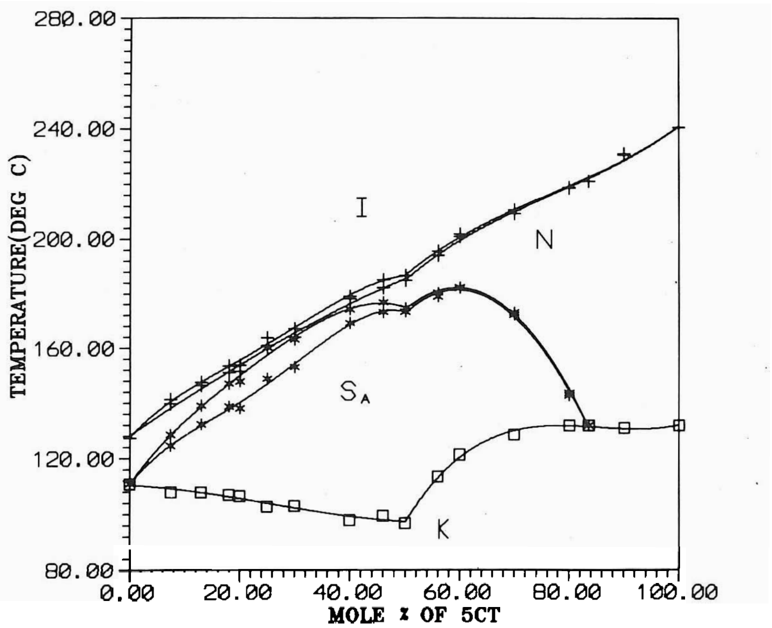

Fig. 1. Phase diagram of binary mixtures of BO10 and 5CT.

phase diagram, which clearly indicates that the smectic A phase which is monotropic in the case of BO10 becomes stabilised as the 5CT content is increased up to some concentration. Indeed there is a peak in the S_A-N transition temperature characteristic of an 'induced' smectic A phase which is known to arise from charge transfer complex formation between the two types of molecules in the mixture [10,11]. Unusually, for a composition near that exhibiting the maximum in the S_A-N boundary, dips in the S_A-N as well as N-I transition points are also seen in this mixture.

Most of our observations on the growth of smectic A liquid crystals have been carried out on mixtures with about 13 to 17 mol% of 5CT, which have a small temperature range of coexistence between the S_A and N phases. In some of the experiments the glass plates were coated with octa decyl triethoxy silane (ODSE) to obtain homeotropic alignment of the nematic phase. Two different solutions having 0.05% (ODSE-I) and 0.5% of ODSE (ODSE-II) respectively were used to get different coverages of the glass plates. Planar alignment was obtained by coating the glass plates with polyimide followed by rubbing in the required direction. All the observations have been made while cooling the samples from the nematic phase.

I. Untreated cells. Observations on a binary mixture with 17 mol% of 5CT (mix A) taken between uncoated glass plates showed characteristic schleiren texture with defects of strength 1 and 1/2 in the nematic phase. As the sample was cooled to the S_A phase a very good homeotropic alignment was obtained.

II. Cells treated for homeotropic alignment. (a) In cells treated with ODSE-I in which

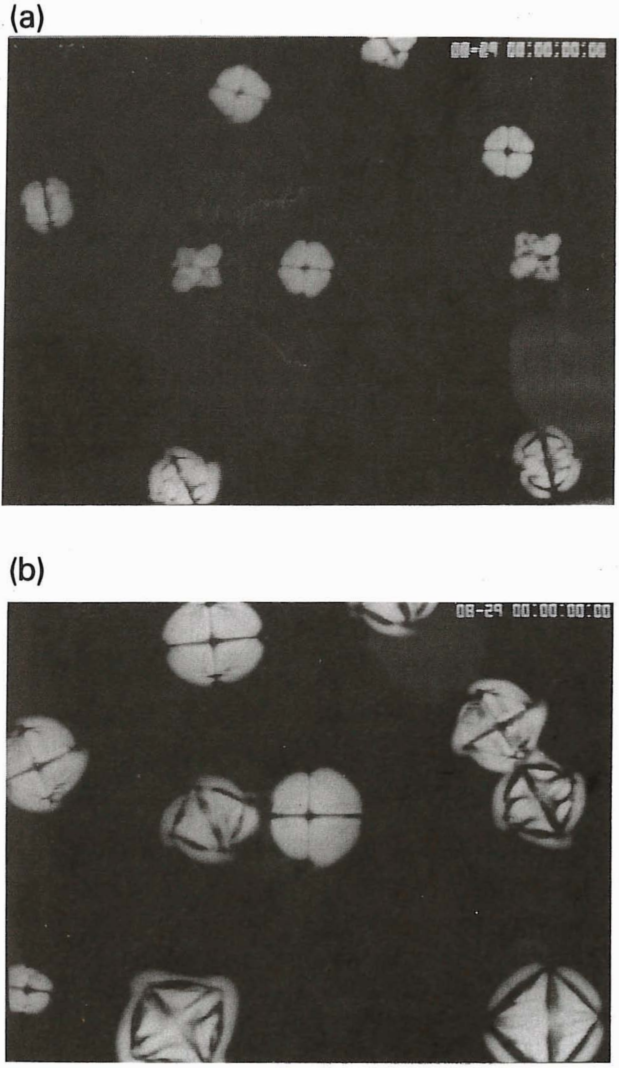

Fig. 2. (a) S_A drops with four lateral sides formed in the homeotropic nematic when mix A was cooled at 0.03°/min. Crossed polarisers (×300). (b) On cooling further by 2°, pairs of drops attract to form doublets. (c) A further cooling by ∼ 1° results in the formation of chains.

the coverage is not dense, a good homeotropic alignment was obtained in the nematic phase. As the sample was cooled at 0.1°/min across the N-S_A transition, the smectic A liquid crystal also had a good homeotropic alignment in most of the field of view. However, a few bright S_A drops which indicates that the director is not aligned along the direction of observation could also be seen. Detailed observations showed that the smectic layers are oriented perpendicular to the interface with the nematic.

(b) In cells coated with ODSE-II which has a dense coverage, the S_A droplets in general do not have the homeotropic texture, but are bright indicating that the director

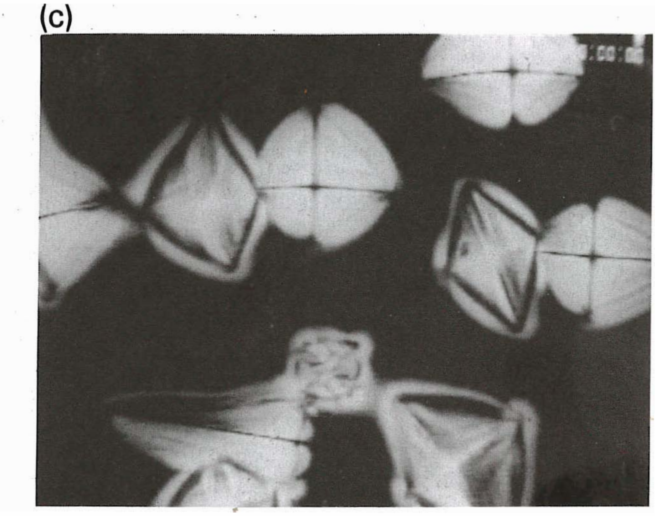

Fig. 2 — continued.

is *not* along the direction of observation (Figs. 2a–c). Indeed the nematic around the periphery also exhibits a bright 'halo' indicating that the director changes its orientation between the N and S_A phases. Further they are attracted to each other such that they form chains (Figs. 3a–c and 4). If the rate of cooling is very low ($\sim 0.03°/\text{min}$), the droplets appear to have 4 lateral sides. The shapes of these drops can vary considerably, some of them having wing-like structures (Fig. 5). As we cool the sample to the S_A phase the whole area is covered by these structures to give rise to a focal conic texture.

III. Dependence on the rate of cooling. In these studies the cell used in II(b) above was cooled from the nematic phase at different rates. It was found that if the rate of cooling is very fast ($\sim 10°/\text{min}$) the homeotropic alignment is preferred. In fact a sudden cooling of the sample from the nematic into the smectic phase results in a complete homeotropic alignment. As expected the N-S_A transition temperature also decreases as the rate of cooling is increased.

IV. Dependence on the thickness of the cell. Preliminary studies were made on a wedge shaped sample with mix A, and a 125 μm spacer placed at one end. The plates had ODSE-II type of treatment. On cooling the sample to S_A at $0.1°/\text{min}$, the thinnest end was found to be homeotropically aligned whereas the thickest end was completely unaligned. There was a gradual increase in the number of unaligned droplets of S_A with increase in thickness. Indeed in a 2.2 μm thick cell, the sample was mostly homeotropic in the S_A phase with a few fan shaped structures. But eventually these also became homeotropically aligned.

V. Dependence on the concentration of 5CT. Binary mixtures with different concentrations of 5CT were studied using ODSE-II coated plates. With only ~ 7.5 mol% of

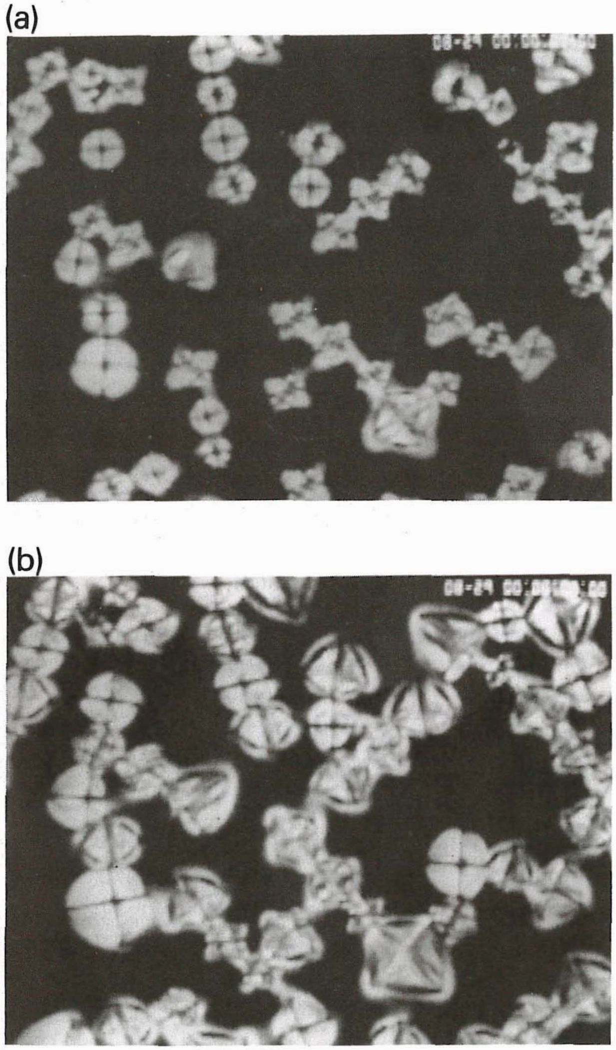

Fig. 3. (a) S_A drops forming chains as mix A was cooled from the homeotropic nematic at 0.1°/min. The drop size is much smaller than in Fig. 2. Crossed polarisers (×300). (b),(c) Merger of chains resulting in an unaligned sample.

5CT a good homeotropic alignment of the S_A phase was obtained. Beyond 25 mol% of 5CT the homeotropic alignment is again preferred, independent of the rate of cooling or thickness of the sample.

VI. Planar boundary conditions. The studies were made on mixtures with about 13 mol% 5CT (mix B). As the sample taken in a 12.5 μm thick cell is cooled slowly from the nematic phase (at 0.03°/min) elliptic droplets are formed (Fig. 6a) the ratio of the major to minor axis in these droplets is of the order of 3 which is a measure of the ratio of $\gamma_\parallel$ to $\gamma_\perp$. Initially the long axes of the droplets make an angle of $\sim$ 10–20° with

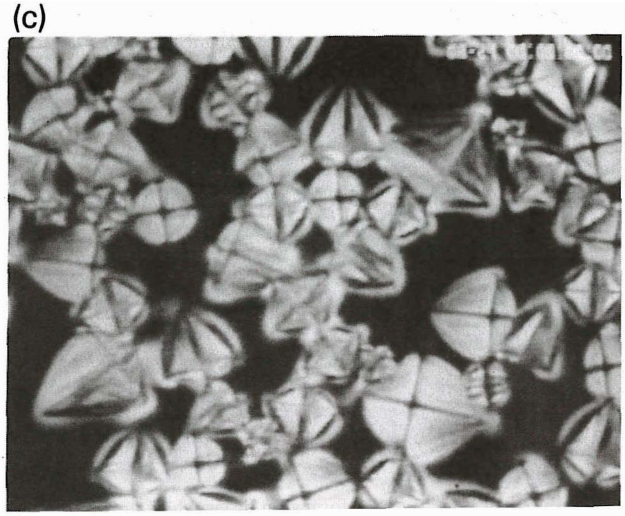

Fig. 3 — continued.

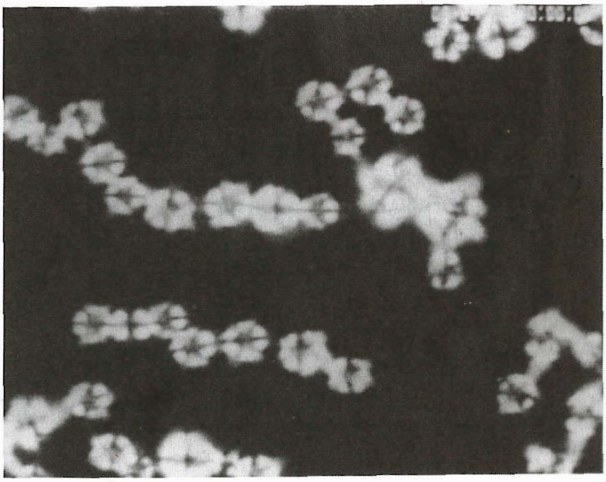

Fig. 4. Mix A cooled at 5°/min from the homeotropic nematic. Chains of longer length are formed compared to samples cooled at slower rates. Crossed polarisers (×600).

the nematic director. Between crossed polarisers a dark band is seen along the centre of these droplets. This indicates that the layers in these droplets are somewhat curved though remaining perpendicular to the interface. As this sample is cooled further and the droplets grow bigger, focal conics can be seen to develop within the droplet (Fig. 6b).

VII. Effect of an AC electric field. An AC field at a frequency of 1 kHz was applied to a sample of the type II(b). The output of a wave form generator (Wavetek Model 395) was controlled through a PC to get a slow variation (~ 0.088 V/s) of the voltage which

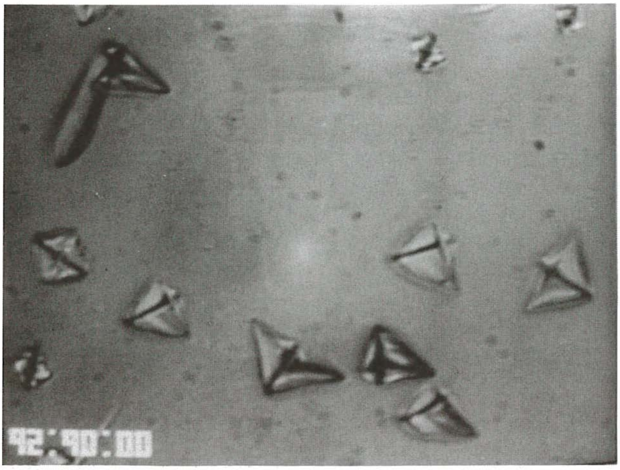

Fig. 5. Wing-like structures (×300) formed in drops which grow independently.

could be either increased or decreased. As the voltage is increased there is an increase in the number of 'sides' of the drop which becomes more circular (Figs. 7a–d). The brightness of the drop also progressively decreases, indicating that the director reorients towards the field as is expected from the positive dielectric anisotropy (≈ 3) of the mixture. At about 80 V the droplet is mostly homeotropic except for the periphery which is bright and has a periodic instability. The number of humps on the periphery is shown as a function of voltage in Fig. 8. If the voltage is increased slowly, there is no apparent motion of the periodic structure on the periphery. However, if the voltage is increased rapidly, this structure moves around the periphery. Even in the former case, small dust particles are attracted towards the smectic drop and are seen to move around the drop, indicating that the medium is not in static equilibrium. The speed of rotation of the dust particle increases with the applied voltage.

If the voltage is decreased at the rate of 0.088 V/s the number of humps decreases progressively. In this case domains having a size similar to that of the humps are seen to develop in the centre of the drop (Figs. 9a–e).

3. Discussion

The ellipticity of the smectic drops separating from the nematic phase in the planar aligned cell indicates that $\gamma_{\parallel} > \gamma_{\perp}$. Usually smectic A liquid crystals prefer to align homeotropically, with the layers parallel to planar surfaces. Hence it may look surprising that the S_A drops do not have this structure when the glass plates are treated with ODSE. We can understand this observation if it is assumed that a microphase separation takes place in the cells, with the BO10 molecules which have a long alkyl chain preferring to be concentrated near the ODSE surface. This increases the 5CT concentration near the centre of the cell. From the phase diagram shown in Fig. 1 the smectic liquid crystal

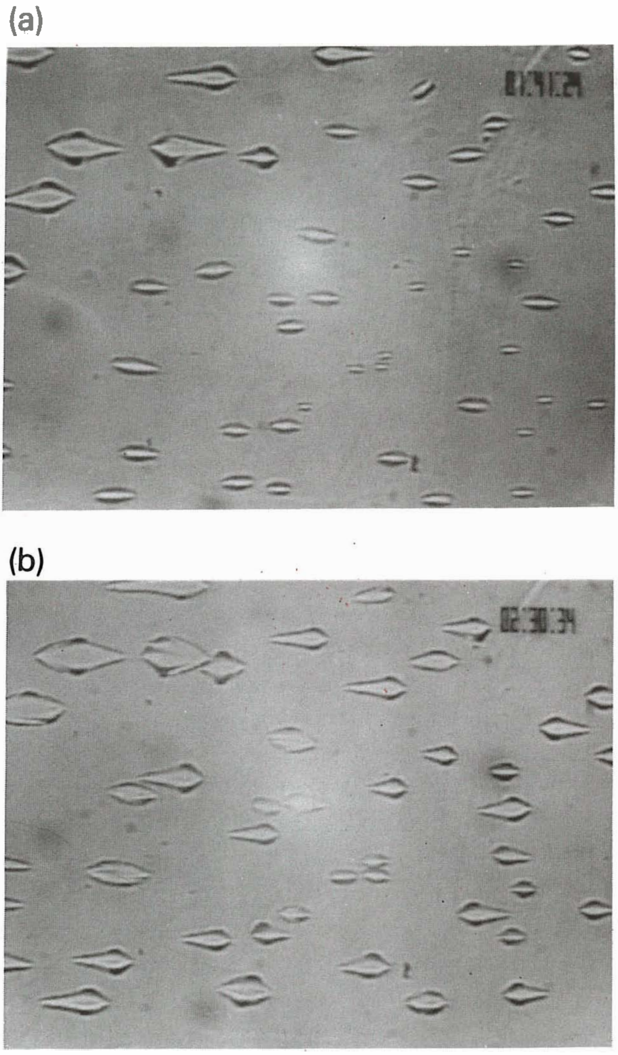

Fig. 6. (a) Mix B cooled at 0.03°/min from a homogeneously aligned nematic. Small elliptic drops, with layers perpendicular to the interface (right hand side of photograph). Polariser parallel to the lower edge of the photograph ($\times 180$). (b) A further cooling by $\sim 1.5°$ leads to the formation of focal conics.

can be expected to nucleate at the centre of the cell.

As both the media across the interface are anisotropic with uniaxial symmetry, we can expect that the interfacial tension depends on the mutual orientation between the smectic and nematic directors. In principle there can be four different values of γ depending on the orientation of the smectic director with respect to the interface-normal, and the orientation of the nematic director with respect to the smectic director. In our binary mixtures, the layers prefer to be oriented perpendicular to the interface, i.e. $\gamma_{\parallel} > \gamma_{\perp}$ irrespective of the orientation of the nematic director. This orientation of the smectic layers is compatible with the formation of focal conic (FC) domains. When the drop size

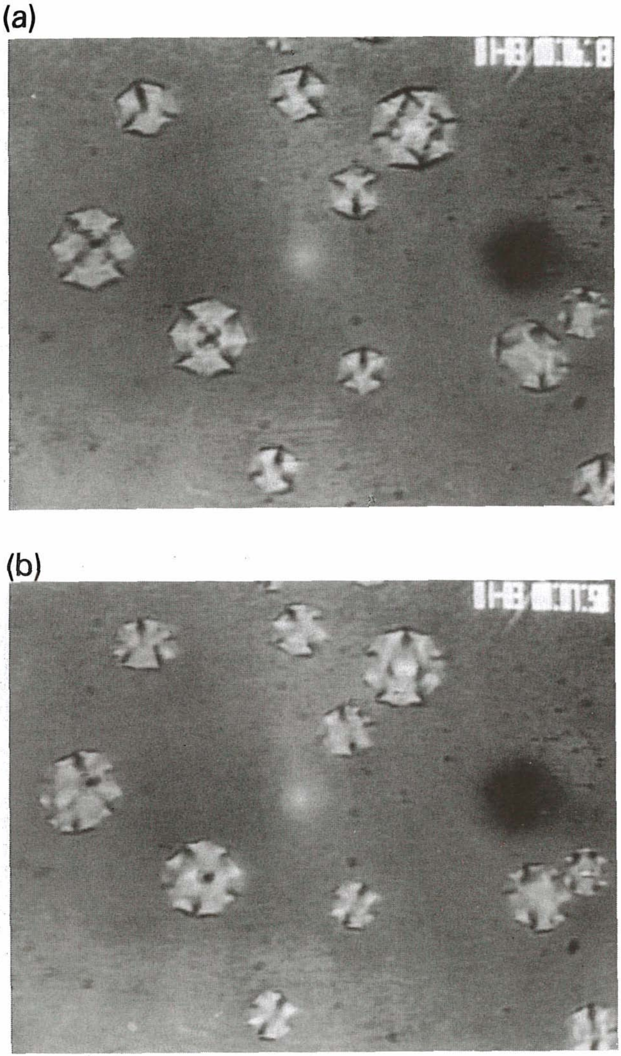

Fig. 7. (a) Mix A, with S_A droplets formed in homeotropic nematic subjected to an AC electric field of 1 kHz. Voltage increased at the rate of 0.088 V/s. Polariser set parallel to the lower edge of the photograph (×300). The voltages are (a) 33.26 V, (b) 42.06 V, (c) 59.4 V and (d) 77.44 V.

is relatively small, i.e. when the width is less than the sample thickness, we can expect to get a focal conic domain with rotational symmetry, i.e. one in which a straight line disclination passes through the centre of a circular disclination which is at the periphery of the domain. The straight disclination is always orthogonal to the nematic director in our samples. From simple geometrical considerations it is clear that in this case the nematic director relaxes to the surface induced homeotropic configuration with all the three distortions, viz. splay, twist and bend. On the other hand, if the straight disclination is parallel to the nematic director, only splay and bend will be involved costing a higher elastic energy. The former orientation of the domain has a cross sectional view with

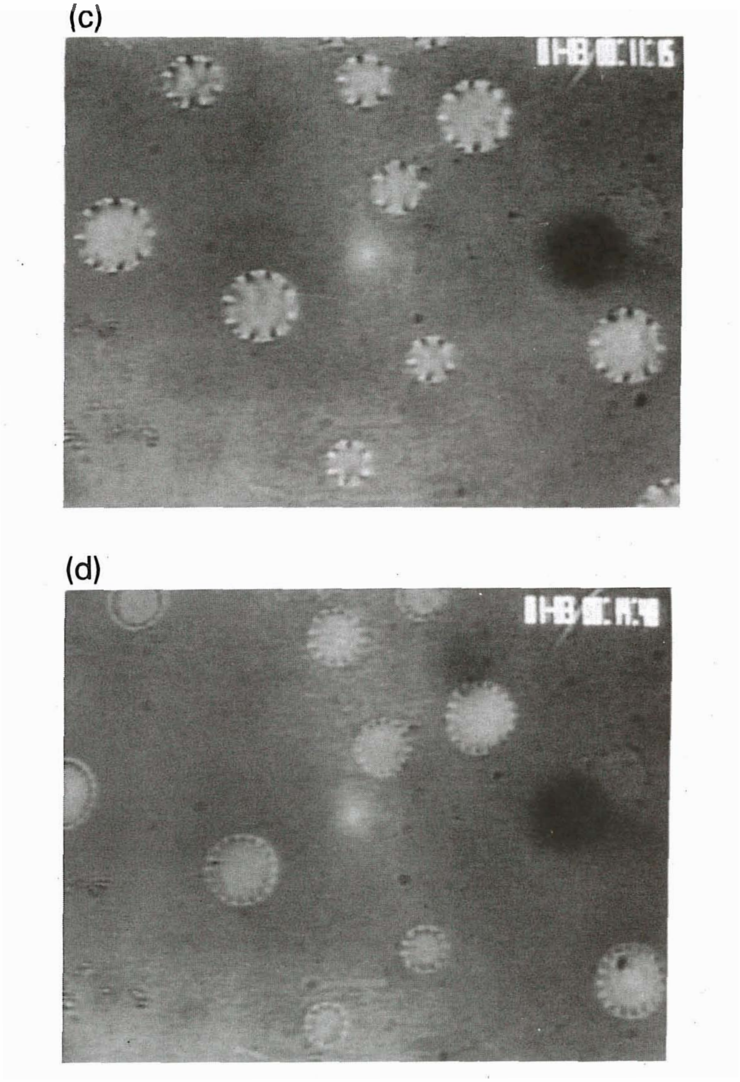

Fig. 7 — continued.

four straight edges.

As the smectic domain grows and the width increases beyond the thickness of the cell the rotational symmetry is no longer possible for the FC domain and the vertical circular disclination changes over to an elliptical one with its short axis along the field of view (Fig. 10). Correspondingly, the straight line changes over to a hyperbola. The domain can be extended over a considerable length of the hyperbola, eventually giving rise to a structure with a wing-like appearance (Fig. 5).

The FC domain shown in Fig. 10 is characterised by a divergence of the smectic director which is positive near the elliptic disclination while it is negative near the two

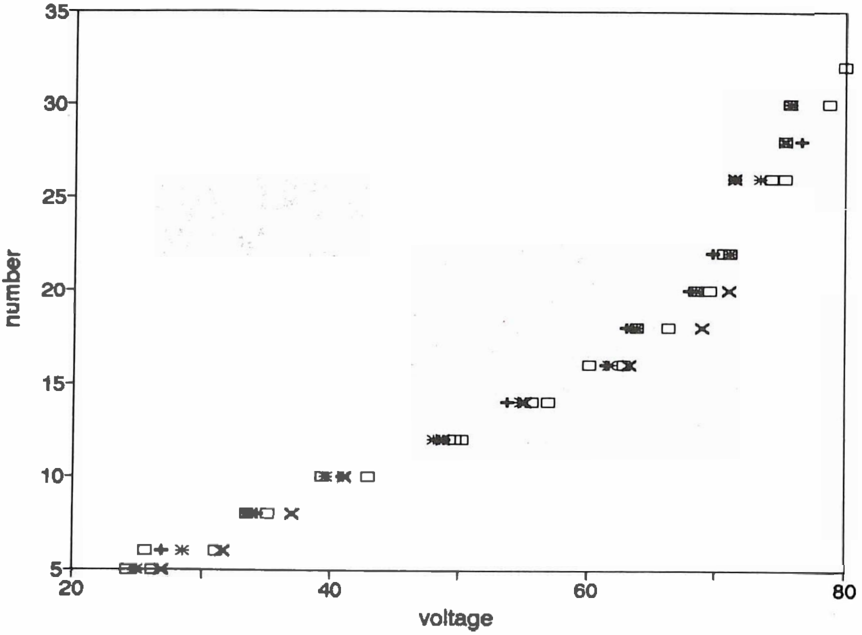

Fig. 8. Dependence of the number of humps on voltage for the sample shown in Fig. 7.

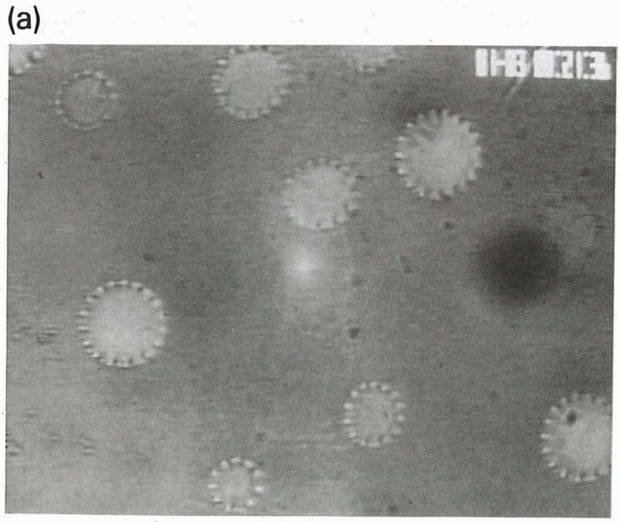

Fig. 9. Same sample as in Fig. 7. Voltage decreased at the rate of 0.088 V/s. The voltages are (a) 46 V, (b) 22.8 V, (c) 15.14 V, (d) 10.48 V.

tips. It is well known that such splayed director fields produce a flexoelectric polarization in the medium [12],

$$\vec{P} = e_1 \boldsymbol{n}(\operatorname{div} \boldsymbol{n}), \tag{3}$$

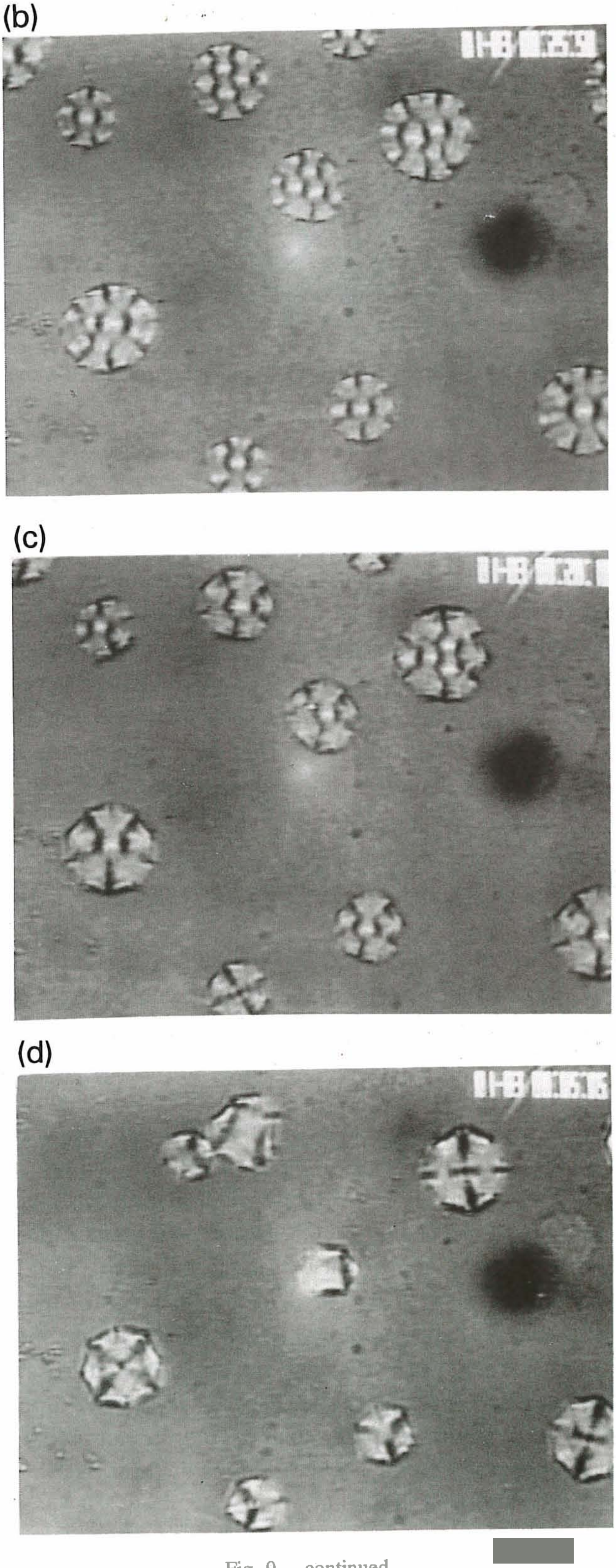

Fig. 9 — continued.

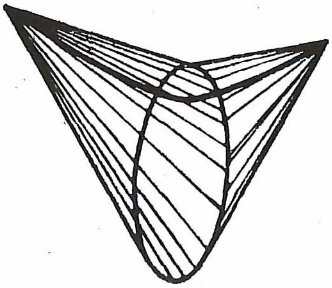

Fig. 10. Schematic diagram of a focal conic domain.

where the flexoelectric coefficient $e_1 \simeq 10^{-4}$ CGS units.

As the flexoelectric polarization is oriented in opposite directions with respect to the interface in different parts of the FC domain, we can expect that two S_A drops will experience an electrostatic attraction when the mutual orientation between them is appropriate. This process also leads to the formation of chains (Fig. 3).

When an electric field is applied, we can expect that the dielectric energy would favour an alignment of the director parallel to the field ($\Delta\epsilon > 0$). If this results in a disc-like domain with a height h and radius R, and with flat layers, the interfacial tension costs additional energy only on the flat surfaces. Ignoring the gain in the curvature energy we can write the energy balance equation for the stability of the structure as

$$-\frac{\Delta\epsilon}{8\pi}E^2(\pi R^2 h) + 2\pi R^2(\gamma_{\|} - \gamma_{\perp}) = 0. \tag{4}$$

If $\gamma_{\|} - \gamma_{\perp} \simeq 10^{-2}$ CGS units and $\Delta\epsilon \simeq 3$, and $h = 10$ μm, the uniformly oriented disc-like structure should be stable at 3 volts. However we do not see such a transformation at all, as the geometrical rearrangement of the layers to get this uniformly oriented structure is not easy. We should note that the nematic which is in the vicinity of the smectic drop is also characterised by $\Delta\epsilon > 0$. The electrical conductivity anisotropy $\Delta\sigma$ can be expected to be negative in view of the smectic-like short range order in the medium. In such a case, an electrohydrodynamic (EHD) instability can set in for this geometry with a splay deformation of the director field in the horizontal plane [13,14]. At 1 kHz we can expect that the EHD instability occurs in the dielectric regime in which the splay curvature changes sign with that of the electric field [13]. The wavelength of this instability is relatively short compared to the thickness of the sample. This is also associated with a flow of the sample which should be in the vertical plane. Our observation of dust particle motion *around* the smectic drops clearly indicates that the EHD motion in the nematic is strongly influenced by the smectic drop. The formation of the corrugated structure at the periphery of the S_A drop and the strong dependence of the wavelength of this structure on E appear to result from this interaction. We are at present investigating this process in detail.

Acknowledgements

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References

[1] P.G. de Gennes, The Physics of Liquid Crystals (Clarendon, Oxford, 1975).
[2] G. Friedel, Ann. Phys. (France) 18 (1922) 293.
[3] J.B. Fournier and G. Durand, J. Phys. II 1 (1991) 845.
[4] P. Palffy Muhoray, B. Bergesen, H. Lin, R.B. Meyer and Z. Racz, in: Pattern Formation in Complex Dissipative Systems, ed. S. Kai (World Scientific, Singapore, 1992) p. 504.
[5] A. Adamczyk, Mol. Cryst. Liq. Cryst. 170 (1990) 53.
[6] R. Pratibha and N.V. Madhusudana, J. Phys. II 2 (1992) 383.
[7] R. Pratibha and N.V. Madhusudana, Curr. Sci. 62 (1992) 419.
[8] R. Pratibha and N.V. Madhusudana, in: Spatio Temporal Patterns in Non-Equilibrium Complex Systems, eds. P.E. Cladis and P. Palffy Muhoray (Addison–Wesley, Reading, 1995) p. 171.
[9] B.K. Sadashiva, Mol. Cryst. Liq. Cryst. 55 (1979) 135.
[10] J.W. Park, C.S. Bak and M.M. Labes, J. Am. Chem. Soc. 97 (1975) 4398.
[11] B. Engelen, G. Heppke, R. Hopf and F. Schnieder, Ann. Phys. 3 (1978) 403.
[12] R.B. Meyer, Phys. Rev. Lett. 22 (1969) 918.
[13] N.V. Madhusudana, Phase Transitions 50 (1994) 177.
[14] K.P.L. Moodithaya and N.V. Madhusudana, Proc. of the Int. Liquid Crystals Conf., Bangalore, December 1979, ed. S. Chandrasekhar (Heyden, London) p. 297.