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Electric field transport of biphilic ions and anchoring transitions in nematic liquid crystals

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Anchoring interaction of MBBA and MBBA + 5CB nematic layers with monomolecular films of CTAB on ITO glass supports is studied by videomicroscopy in the presence of an electric field. Planar–planar or homeotropic–homeotropic electrode substrates are used to make the nematic cells. The substrate symmetry is broken by coating only one electrode with self-assembled CTAB film. In a DC electric field we observe some new effects: (i) polarity-dependent breaking of anchoring and switching to two oblique states in dielectrically stable planar cells; (ii) a polarity-dependent flow-induced metastable anchoring transition in homeotropic cells to a planar or tilted alignment after the field is switched off. These results are discussed in terms of a surface transition assisted by electric transport of biphilic CTAB ions and by a surface memorization of the flow-induced planar alignment.

1. Introduction

Molecular layers on solid supports were used for a long time as orienting substrates for nematic liquid crystals (NLC). The first well-defined and precisely characterized system of this type comprised the nematic material MBBA and a molecular film of cetyltrimethylammonium bromide (CTAB) on silica and on glass [1–3]. The CTAB films were self-assembled by dipping the substrates into water solutions of the surfactant CTAB at different concentrations and pulling them out with different speeds. The adsorption isotherms of CTAB were established [1]. Later on, a remarkable dependence of the type of anchoring of MBBA on the surface density of CTAB was established: planar anchoring below a certain critical density (corresponding to about 18 per cent area coverage, if one assumes a $0{\cdot}2\,\mathrm{nm}^2$ area per homeotropic, all-*trans*-CTAB molecule) and homeotropic anchoring above this critical density [2, 3].

One could then imagine that if some means of gradual variation of the surface density could be employed, an anchoring transition could be achieved between planar and homeotropic orientation. In the present paper, an attempt is made to exploit the ionic nature of CTAB in this respect by means of a DC electric field.

In § 2 of this paper, materials and methods are presented; experimental results are then reported in § 3 and discussed in § 4, followed by a brief conclusion.

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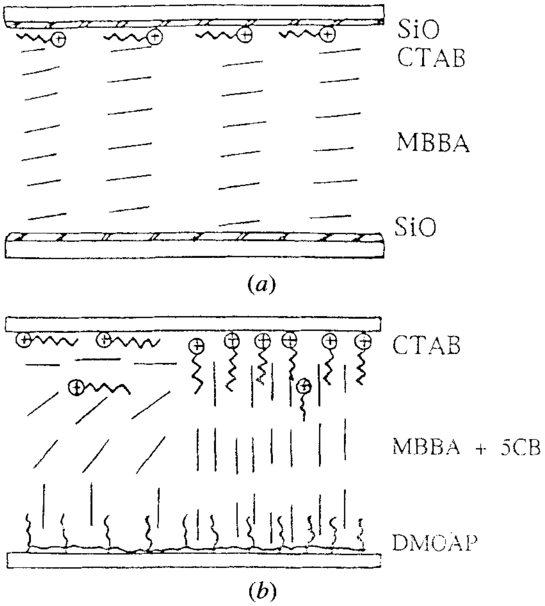


Figure 1. Two basic experimental geometries of the nematic layers investigated: (*a*) planar SiO-oriented layer with the top plate covered by an expanded CTAB film (*c.* 1 $nm^2 mol^{-1}$). (*b*) homeotropic silane (DMOAP)-oriented layer with one half of the top plate covered by an expanded CTAB film (*c.* 1 $nm^2 mol^{-1}$). An even more expanded coverage is indicated on the other half (see text).

2. Materials and methods

Basically, nematic layers of MBBA ($T_c = 46{\cdot}1°C$) were studied throughout. In some cases, a dielectrically compensated mixture of 98·05 wt% MBBA + 1·95 wt% 5CB (Merck Limited) with zero dielectric anisotropy was used. The nematic material was sandwiched between two conducting ITO-coated glass plates with different treatments of the electrode surfaces. In order to localize easily the plate where the anchoring transition takes place, only one electrode surface was treated with CTAB. Mainly two types of asymmetric electrodes in symmetrically textured cells, 'planar' or 'homeotropic', were investigated (see figure 1):

(i) *Planar* (figure 1 (*a*)): planar anchoring, i.e. nematic orientation parallel to the plates, was introduced by SiO evaporation at 60° giving a 45 nm thickness of evaporated layer. CTAB was then applied to the top electrode of the LC cell only (see below), just over the SiO coating, thus resulting in a small initial tilt.

(ii) *Homeotropic* (figure 1 (*b*)): homeotropic anchoring corresponds to nematic molecules oriented normal to the plates. To achieve that, the lower electrode was covered by a silane (DMOAP, Thomson CSF) by dipping the plates in a 1 per cent solution of DMOAP in an isopropyl alcohol/water mixture (9 : 1), washing them in water and then curing them at 110° under N_2 for 1 h. The CTAB monomolecular film was again applied to the top electrode only. In some cases only half of this electrode was covered by CTAB for the sake of comparison.

The deposition of CTAB on the ITO surfaces was carried out by dipping them in a 2×10^{-5} M *N*-cetyl-*N*-*N*,*N*-trimethylammonium bromide (Merck 99 per cent p.a.) in ultra pure water (Millipore, 18 MΩ cm). The plates were withdrawn either using a self-made device or manually with a speed of 1 cm min^{-1}. These conditions correspond to the second plateau of the liquid–vapour isotherm of Saraga *et al.* where a surface CTAB density of about $9 \times 10^{13}\,\mathrm{mol\,cm}^{-2}$ is to be expected [1–3]. Care was taken to use only plates which emerged completely dry from the CTAB solution. In the case of some remaining droplets, the concentration of CTAB would be increased locally after their drying.

Liquid crystal cells were assembled with 3·5 μm mylar spacers on triple screw holders permitting an interferometric adjustment of electrode parallelism and a measurement of the empty cell thickness. Cells were filled at room temperature by capillarity. The expected type of anchoring was then observed some time after filling, typically a minute. Most experiments were performed at room temperature. In some cases a Mettler FP5 heating stage was used for measurements at elevated temperatures.

The observations were made using a Leitz Laborlux 12 Pol polarizing microscope (Leitz, Germany) equipped with a photomultiplier set-up (Leitz) for registration of localized transmitted light intensity and a video camera (Sony, Japan). The light intensity signal was registered as a function of time by a Textronics 2430 digital memory scope with a Hewlett–Packard printer. The video frames were recorded on a U-matic SP Sony video recorder and printed on a Polaroid TX 1000 colour printer. Electric pulses for cell excitation were provided by an Exact Model 7050 function generator (Exact Electronics Inc., USA) and amplified by an NF Electronic Instrument 4005 high speed power amplifier (NF Corporation, Japan).

3. Experimental results

3.1. *Polarity-dependent anchoring breaking in planar nematic layers*

When planar MBBA layers oriented by SiO, with a CTAB monolayer deposited on the top electrode, were subjected to a DC voltage or to opposite polarity square pulses or sine waves of very low frequency (*c.* 0·02 Hz), the following phenomena were observed depending on the voltage amplitude. At zero voltage, the initial orientation was almost planar and between crossed polarizers appeared completely black when the easy direction of SiO coating was parallel to either polarizer or analyser (as in figure 2 (*b*)) Using a sine wave pulse, at low voltage amplitude (below 10 V), only weak variations of the initial tilt of the planar texture director (relative to the plates) could be observed in the interference mode of observation (easy axis at 45° with respect to the crossed polarizers, monochromatic green light and using a 3λ compensator). On further increasing the voltage amplitude to about 15 V (frequency of 0·2 to 1 Hz), a faint set of striations appeared, running both normal and parallel to the easy direction. They could be noticed if the field of view was darkened by the first interference fringe of the compensator. The specific appearance of the domain pattern was polarity dependent. These slight variations of the overall tilt and modulated structures of low tilt amplitude are not however the main topic of the present paper.

When the easy axis of the nematic texture is parallel to the polarizer, the initial low-voltage modulated structure is not visible. In this geometry, applying a DC voltage of − 12 V at the top plate one can observe, after a delay of 25 s, a dramatic structural transition: it starts with a pronounced nucleation of ‘umbilics’ (central defects) which eventually merge and result in a breakdown of the planar anchoring (see figure 2 (*a*)). At the opposite polarity of + 12 V, no change could be observed even after a couple of minutes. Using back negative polarity, and increasing the voltage amplitude to

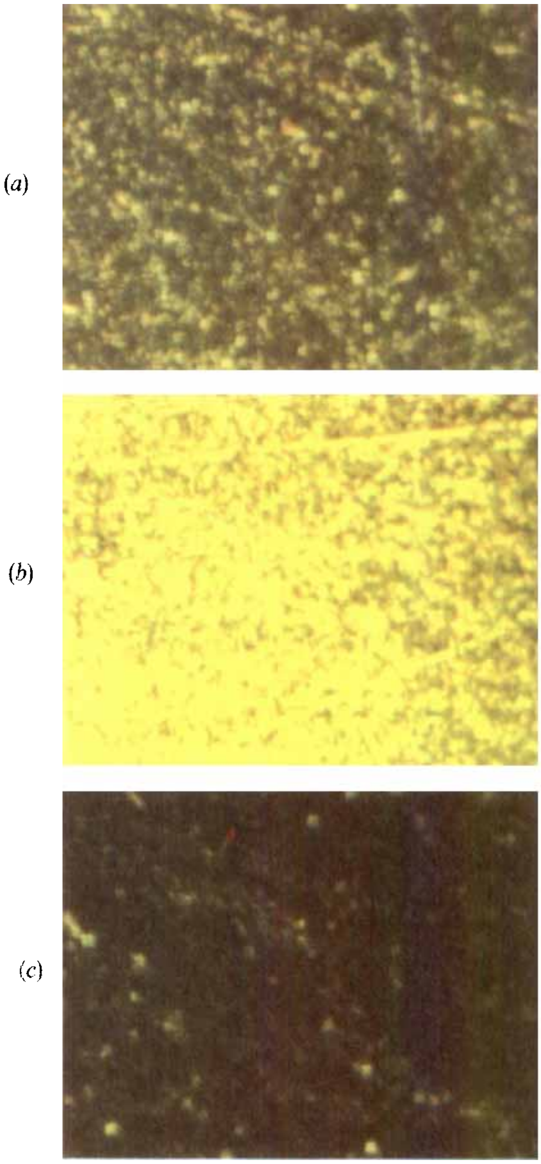


Figure 2.

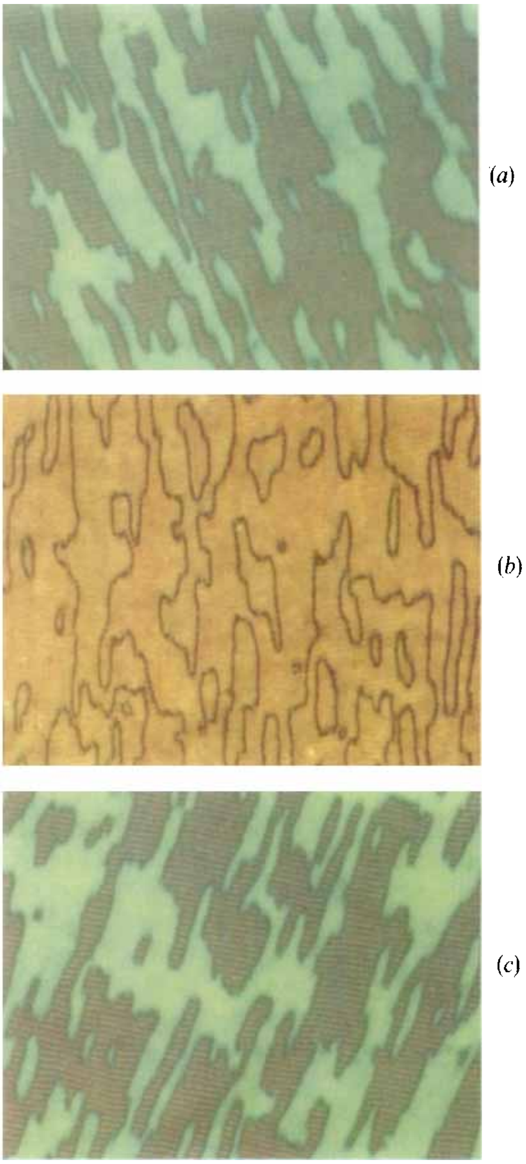
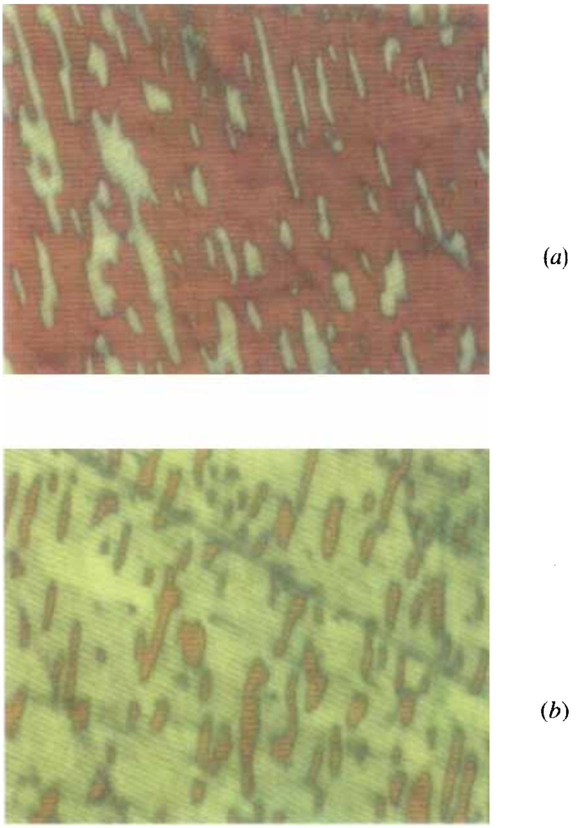


Figure 3.

Figure 2. Polarity dependent anchoring transition in planar 3·3 μm SiO–MBBA–SiO (CTAB) cells. The easy axis is vertical. (*a*) − 12 V DC, 25 s after pulse on, onset of the transition; (*b*) − 23 V DC (CTAB-covered plate negative), pulsed excitation 0·03 Hz, duty cycle 0·5, 5 s after pulse on: breaking of planar anchoring; (*c*) + 23 V DC (CTAB-covered plate is positive), pulsed excitation 0·03 Hz, duty cycle 0·5, 16 s after pulse on: planar orientation is stable.

Figure 3. Experimental conditions are the same as for figure 2. Two sets of oblique domains above the threshold in planar cells. (*a*) − 12 V DC., rotation of the microscope stage − 25° to the left, demonstrating the twist sense in one set of the two oblique domains; (*b*) − 12 V DC, easy axis is vertical; (*c*) − 12 V DC, rotation 19° to the right, demonstrating the twist sense in the second set of oblique domains. Note in (*a*), (*b*) and (*c*), the zig–zag aspect of Williams rolls in the two sets of domains, another indication of the twist sense.


(a)

(b)

Figure 4. Another set of oblique domains obtained after reversing the polarity of the cell from figure 3 by applying + 20 V DC and waiting for several minutes. Other experimental conditions are the same as for figures 2 and 3. (*a*) + 14 V DC, rotation of the stage − 28° to the left; (*b*) + 14 V DC, rotation of the stage + 10° to the right. Note completely different domain pattern compared to figure 3.

− 23 V, the time delay of anchoring breaking is reduced to 5 s (see figure 2 (*b*)). The opposite polarity did not produce any change in more 3 times this length of time (see figure 2 (*d*)). Going back to negative polarity, we rotate the stage to improve the contrast. Figure 3 (*a*) to (*c*) demonstrates that after breaking of the anchoring, the initially planar layer appears to split into two sets of complementary domains, with opposite twisted orientation. The twist could be proved by rotation of the microscope stage until one (or another) of the sets became dark and also by observation of the 'Williams rolls' [4] orientation in each one of the two sets (see figure 3 (*a*) and (*c*)). These rolls are well known to align perpendicular to the nematic director. Finally, it also turned out to be possible to induce a surface transition by applying a higher positive voltage at the top plate (+ 18 to 20 V) and waiting for several minutes. Now the transition seems to take place at the bottom cell electrode. The pattern of twisted domains is completely different (see figure 4 (*a*) and (*b*)). After this positive polarity-induced surface transition,

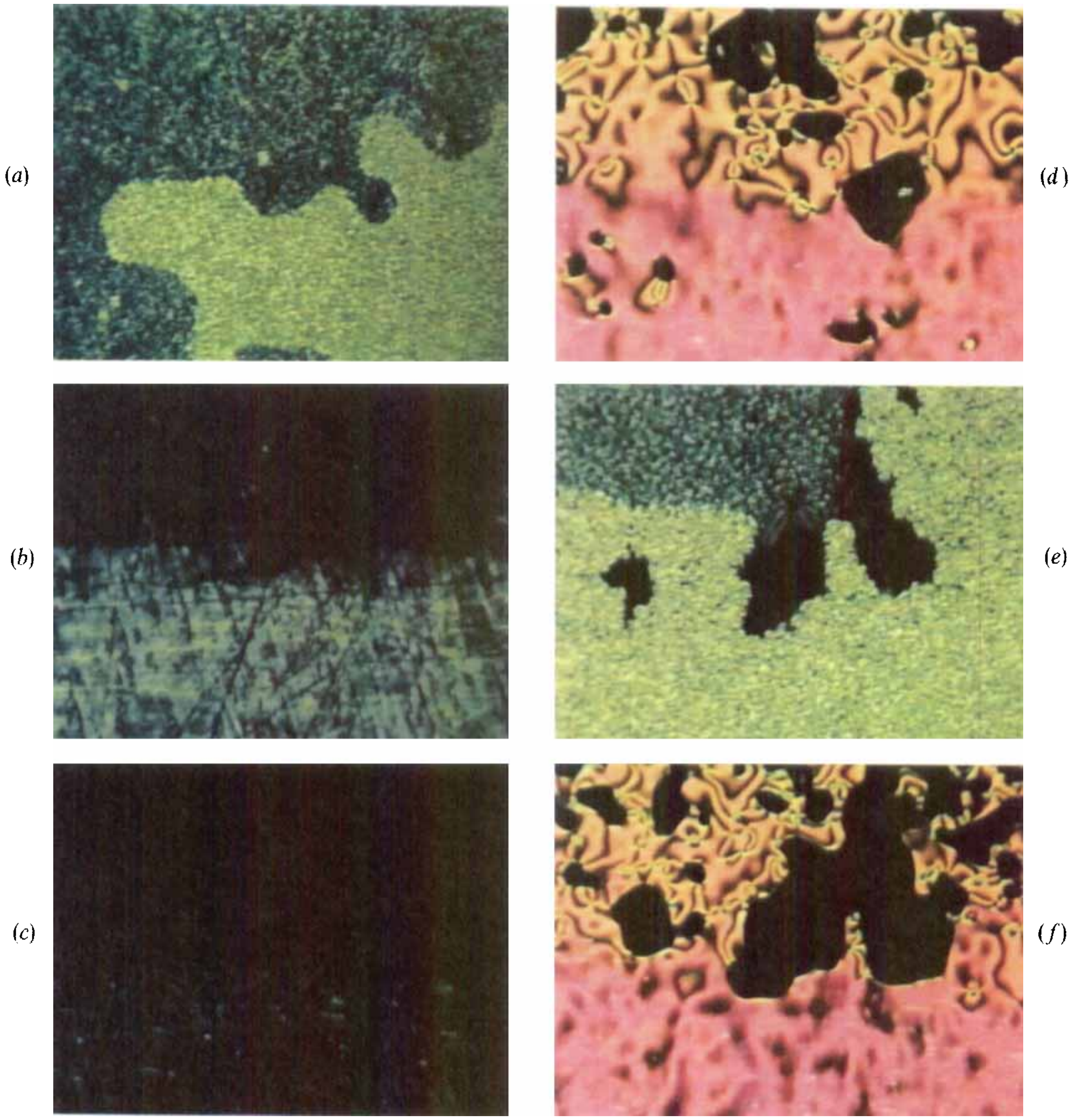


Figure 5. Anchoring transitions in a homeotropic layer of MBBA + 1·95 wt % 5CB, thickness 4·4 μm. Top electrode half covered by a CTAB monolayer. Bottom electrode silane-coated. (*a*) + 12 V at the top electrode, 30 s waiting time. Turbulent hydrodynamic motion. The brighter area is already switched to a planar orientation; (*b*) 0 V, upper half is CTAB-covered and homeotropic, and the lower part is not covered and defected homeotropic; (*c*) − 12 V at the top electrode, 5 min waiting time. No hydrodynamics, and improvement in the homeotropy of the lower part; (*d*) Field-off after + 12 V excitation for 1 min. Anchoring transition in both parts: tilted and conical anchoring in the CTAB-covered area, and planar anchoring in the uncovered area; (*e*) + 11·6 V, 45 s excitation time; (*f*) Anchoring transition just after field-off (compare with figure 5 (*e*)). After field-off non-switched homeotropic regions start to expand at the expense of the switched regions, resulting in complete recovery of the overall homeotropy in 10–15 s over the top half and in 25–30 s over the bottom half.

we try again to induce the surface transition using negative polarity. At the level of − 12 V, the cell remains stable. To restore the initial polarity of the surface transition, we must again increase the voltage and wait for a longer time. In other words, the cell polarity, which was defined by the CTAB initially coated plate, becomes now dependent on the electrical history of the applied stimuli.

When the field is turned off, a relaxation of the oblique domains back to the planar orientation is observed in a relatively short time interval (*c.* 1 s).

3.2. *Anchoring transition in homeotropic layers*

When homeotropic nematic layers of MBBA + 5CB (dielectrically compensated) are subjected to a DC voltage one could observe at first electrohydrodynamic motion of the fluid, strongly dependent on the voltage polarity (see figure 5 (*a*), (*b*), (*c*). When the top CTAB covered electrode is positive, electrohydynamics start at about + 8·0 V, while a negative voltage at the top electrode, no electrohydrodynamics could be observed in this voltage range. This strongly asymmetric hydrodynamic behaviour could be attributed to the presence of mobile ions of one given sign, coming from one given electrode and flowing in the nematic. We observe then the current–voltage characteristics of this cell showing rectification. For positive voltages the current is large, but is blocked in the negative range of voltages (not shown). At negative potentials, in the absence of current and flow, the homeotropic orientation appears stable (see figure 5 (*c*)) and is in fact improved with respect to the voltage-free state (see figure 5 (*b*)). Since the dielectric anisotropy of the material is compensated, such an effect must result from an electrically induced change in the easy direction of the anchoring. On the contrary, the hydrodynamic turbulent flow, produced by positive potentials, is capable, after a sufficiently long time, of producing an anchoring transition (bright areas on figure 5 (*a*) and (*e*)). After switching off the field, one could see that the resulting flow-induced anchoring is a tilted conical anchoring, in the CTAB-covered area (resulting in a Schlieren texture) and almost a planar one in the non-covered area (judging from the higher interference colour: figure 5 (*d*) and (*f*)). This transition is metastable: the non-switched homeotropic area after switching off the field expands by means of moving surface defect lines at the expense of the switched area, and within a time interval of about 30 s, the homeotropic orientation is restored everywhere. This relaxation proceeds faster over the CTAB-covered area (10–15 s) than over the uncovered area (25–30 s). The expanding homeotropic domains during the field-off period originate mostly from the CTAB-covered area.

Using pure, uncompensated MBBA, the same behaviour is observed as with the compensated mixture, namely the same surface transitions and different surface orientations in regions with or without CTAB coating. We can now change the orientation of the nematic texture by using an AC field coupled with the negative dielectric anisotropy, which tends to align the nematic to be planar instead of homeotropic, above the well-known [4] Fréedericksz threshold. We are able in this way to slow down or even stop the expansion of homeotropic domains by applying an AC voltage, above the Fréericksz transition threshold, to MBBA filled cells, so that homeotropic domains become tilted.

We are now interested in the turn-on time of the anchoring transition. Figure 6 displays the dependence of these turn-on times on the applied voltage. Several cell areas and experimental protocols were investigated and attempted in order get an insight into the mechanism of the observed phenomenon (see § 4). As previously reported, no transition is visible below the 8 V hydrodynamic threshold. Just above this threshold the turn-on times are very long, much longer than those of any other electro-optics effect in NLC. They tend to decrease on increasing the voltage above 8 V (in line with the increase in the flow velocity), but at higher voltages saturate at 20 s.

Since the appearance of this transition seems closely coupled to the onset of flow, an attempt has been made to influence its threshold by changing the liquid crystal bulk orientation, with the same homeotropic treatment for the plates. This is based on the fact that the nematic vortex flow is self-impeding with homeotropic orientation and enhanced with planar alignment. To this end a pure MBBA sample was subjected

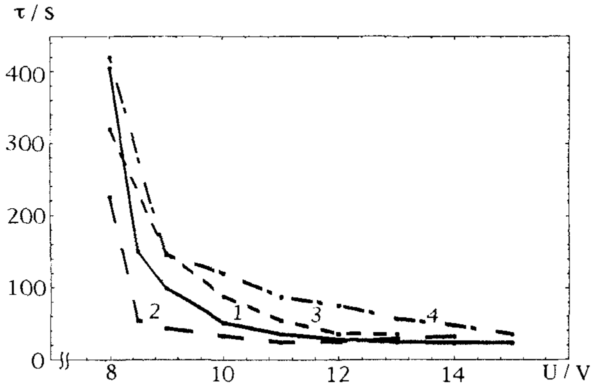


Figure 6 Turn-on times for the appearance of the anchoring transition as a function of applied voltage in a silane-CTAB homeotropic layer of MBBA + 1·95 wt % 5CB, layer thickness 4·4 μm, DC excitation, positive voltage at the top CTAB electrode; various regions of the electrode are designated: (1) CTAB-covered area, increasing the voltage; (2) uncovered area, keeping the cell under the same negative voltage for 5 min after each measurement; (3) uncovered area, cooling the cell for 5 min after each measurement; (4) CTAB-covered area, decreasing the voltage and cooling for 5 min after each measurement.

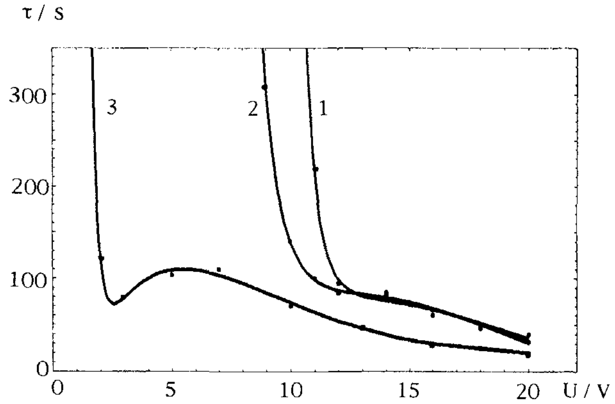


Figure 7 Turn-on times for the appearance of the anchoring transition as a function of the DC voltage in a silane-CTAB homeotropic layer of MBBA, layer thickness 5·0 μm for different values of the AC bias voltage. All curves are obtained with a positive voltage on the top CTAB electrode, when decreasing the voltage. (1) no AC voltage; (2) 4·9 V_{rms} 1 kHz AC bias (slightly above the Fréedericksz threshold of 4·1 V_{rms}; (3) 20 V_{rms} 1 kHz AC bias.

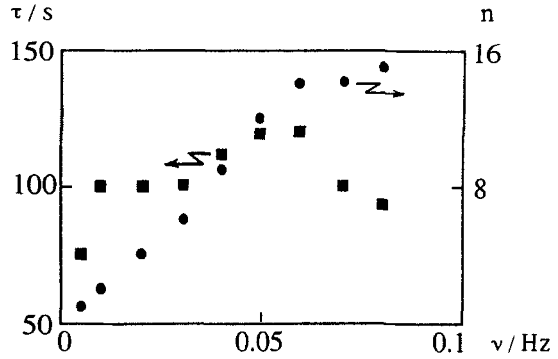


Figure 8. Cumulative effect of unipolar pulses on the anchoring transition. Silane–CTAB homeotropic layer of MBBA + 1·95 wt % 5CB, layer thickness 4·4 μm. Pulsed excitation with unipolar pulses of 8·7 V, duty cycle 0·5 and variable frequency. Circles represent the number of pulses (*n*) necessary to produce the anchoring transition: squares represent the total duration (*t*) of the positive voltage. Between the measurements the sample was kept for 5 min under unipolar negative pulses of − 9·0 V with the same frequency, producing *no* anchoring transition.

simultaneously to DC and AC voltages, where the AC voltage exceeded the Fréedericksz transition threshold (4·1 V_{rms} for that particular cell (see figure 7). For this sample, in the absence of AC field, the DC flow threshold is 10 V. Indeed, by 4·9 V_{rms}, 1 kHz AC bias, the DC flow could be reduced from 10 V to 8 V and even down to 1 V using 20 V_{rms} AC bias. In this way it was possible to observe the anchoring transition at lower voltages. The turn-on times, however, remained long (see figure 7).

A very important point for understanding the nature of this phenomenon is the observation of the cumulative effect of unipolar pulses on the anchoring transition (see figure 8). By pulsed excitation of an MBBA + 5CB mixture with positive pulses of 8·7 V and variable frequency, the number of pulses necessary to produce the anchoring transition was almost a linear function of the frequency, yielding for the total duration of the positive voltage (sufficient to induce the transition) a practically constant value of 105 ± 3 s at each frequency (for comparison, with DC excitation, this time was 75 s, see figure 8). Another sample of pure MBBA, with positive 14 V unipolar pulses in the frequency range 0·01–0·08 Hz, required a total duration of the positive voltage of 163 ± 3 s (not shown). The DC turn-on time in that case was 85 s (see figure 7). The ‘memory’ effect, so to speak, associated with the flow seems more effective in the compensated MBBA + 5CB mixture.

4. Discussion

As mentioned above (Material and methods), an area density of the self-organized film of CTAB in the order of 9×10^{13} mol cm^{-2} is to be expected from a comparison of our deposition conditions with those of Saraga *et al.* [1, 3]. Such a density should suffice to produce a homeotropic orientation. However, after filling the cell with the nematic, some of the CTAB will probably dissolve in the liquid crystal, reducing the surface density. Such a reduction is expected to be higher from the SiO-coated surface because of its roughness which reduces the adsorption energy of the CTAB molecules. The remaining number of molecules is insufficient to overcome the tendency for planar anchoring on the SiO grooves. This could only produce some finite initial tilt and weaken the strength of the planar anchoring, and so allow the manifestation of linear and gradient flexoelectric surface torques. The latter are probably responsible for the observed low field, polarity-dependent tilt variations and longitudinal domain patterns [5, 6].

Dissolved CTAB biphilic ions carrying a positive charge may just be the source of movable positive carriers which could explain the observation of a rectifying type of I–V curves at negatives voltages, and the polarity-dependent electrohydrodynamic flow. Screening of negative surface potentials by positive biphilic ions favours their readsorption on the electrode surface. We believe that the CTA^+ ions, responsible for the surface homeotropic orientation at density, are also responsible for the DC current, and not the Br^- ions. (The arguments are the following: The small and completely polar Br^- ions are strongly attracted to opposite charges inside the conducting ITO layer. They are also weakly soluble in the bulk nematic. On the contrary, the CTA^+ ions are more bulky, the N^+ charge is separated from opposite charges by the 3 methyl groups and so is more weakly attracted, and these biphilic ions are more easily solvated in the nematic through their aliphatic tails.) In the case of the SiO coated surface, the competition between the planar anchoring tendency due to the grooves and the homeotropic anchoring tendency of CTAB above a critical surface density apparently leads to a surface disorientation of the nematic sufficient to drive an 'ordoelectric' surface transition, as discussed for instance in [6] and [7]. In the case of surface disorder produced by a specially chosen SiO topography, such a transition is manifested in broken planar anchoring and the appearance of two oblique states with the same tilt and opposite twist sense with respect to the initial easy axis orientation [7, 8]. This is very similar to our present observations (c.f. figure 3).

Let us stress here that the breaking of the surface anchoring, after accumulation of enough nucleated umbilics (taking many seconds), drives the volume flow of the Williams rolls, and not vice versa. Field-off relaxation is relatively fast because of the degeneration of the twist sense and the equal number of left and right-handled domains.

Thus, the anchoring breaking in planar layers is consistent with the idea of a field-induced, polarity-dependent variation of surface density of biphilic ions. Positive surface potentials will repel CTA^+ ions from the top electrode enhancing their desorption. The observed reversal of the cell stability by a high positive voltage after a sufficiently long time can then be explained by a transportation of the biphilic ions to the bottom cell electrode and the subsequent build-up of a more dense adsorption layer of CTAB-ions over its surface, sufficient then to break the anchoring on the bottom SiO-coated plate.

The anchoring transition in homeotropic CTAB cells is also consistent with the idea of a reduction in the surface density of CTAB by positive potentials below the critical value necessary to switch the anchoring to planar. However, since the turn-on times are at least 20 times longer than for the planar cells, and, moreover, the onset of vortex flow seems to be very important (no flow—no transition), another mechanism must be invoked: a flow-assisted adsorption of (NLC and CTAB) molecules in a planar orientation over the surface. The role of flow is therefore to 'brush' the surface molecular layer long enough in order that a planar orientation of a sufficient number of molecules is memorized. This explains well the existence of a threshold in this transition, closely related to the flow-onset threshold (see figure 5) and also the decrease in turn-on times with increasing voltage because of the increased orienting action of the shear flow (flow velocity $v_{\rm flow} \sim V - V_{\rm th}$. Assuming that the desorption process is slower than the adsorption process, we can also easily explain the cumulative effect of unipolar pulses as being related to the existence of a critical density of planar adsorbed molecules, necessary to break the homeotropic anchoring. Figure 5 (*d*) and (*f*) demonstrates that planar adsorption is better and memorized for a longer time over a part not initially covered by CTAB (where an expanded CTAB layer is probably formed after filling the cell). Such an adsorption–desorption mechanism was earlier advanced by Vetter *et al.* [9, 10], to explain planar memory alignments of NLC over non-treated PVA surfaces. The desorption process was, indeed, slower than the adsorption process.

We checked also another possibility based on the resemblance of the conical anchoring over the CTAB self-organized monolayer to that observed on compact Langmuir–Blodgett films of barium arachidate on mild heating [11]. The idea that heating of the conductive NLC may suffice to produce the necessary temperature increment was tested by prolonged cooling of the sample by a stream of cold air between two measurements. Although such a procedure did produce some increase in the turn-on times compared to the uncooled case (see figure 6, curves 3 and 4), it failed to reveal a $\tau \sim 1/V^2$ non-threshold behaviour instead of the $\tau \sim 1/(V - V_{th})$ threshold behaviour. On the other hand, keeping the sample at a negative voltage between the measurements reduced substantially the turn-on times in the part not treated with CTAB, consistent again with a field-associated increase of CTAB surface density.

Separate experiments with a Mettler heating stage indicated that a temperature induced anchoring transition in the CTAB–MBBA system can only be observed at 0·1°C below the clearing point (46·1°C). Keeping the sample at 45·8°C did not lead to any important difference in the field-induced anchoring transition, apart from the increased flow velocity due to the reduced nematic viscosity. Thus, the two anchoring transitions, the field-induced and the temperature-induced, appear independent of one another.

To explain the conical anchoring at the CTAB covered plate, after the action of the positive field, we give the following argument. Because of the DC current, and the brushing from the mechanical flow, the actual CTAB density after the field action ought to be reduced. The surface ordering, a combination of the spontaneous planar orientation of the nematic, in small areas between molecular patches of CTAB, and the homeotropic orientation on CTAB, should result in a lower average surface order parameter. The surface induced gradient of order parameter is known to drive the layer, through the order electric polarization [7, 8], to a conical anchoring.

The metastable, long-term relaxation with field-off (see figure 5) corresponds to the idea of a surface anchoring transition in the switched domains. They actually disappear because of the growth of their homeotropic environment (of lowest elastic energy), not by an internal relaxation of their own orientation. Residual non-switched homeotropic domains could never be avoided completely under the present experimental conditions. However, by tilting them with an AC field, we could stop their expansion into the switched domains and keep the latter for an indefinitely long time (see above).

The area of ITO not covered by CTAB (with a possible lower concentration of transported CTA^+ ions) displays a marked bistability between non-ideal homeotropic and planar anchoring. The hydrodynamic, flow-induced anchoring transition, as compared to results from a previous study of an in-plane anchoring switching by flow [12], can be spread over a large area in a more or less uniform manner. This aspect of the observed transition might be of some practical interest.

5. Conclusions

Anchoring transitions in planar and homeotropic nematic layers in contact with self-organized monomolecular films of ionic amphiphiles have been observed. Results are consistent with a novel mechanism involving an electric transport of anchoring action by a polarity-dependent transport of biphilic ions. They also confirm, for a flow alignment regime, an adsorption–desorption mechanism of surface memory alignment, as proposed by other authors [8, 9]. The hydrodynamic flow is now able uniformly to switch a large area of ITO surface from a homeotropic to a planar state.

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