Electrooptic and Dielectric Spectroscopy Measurements of Binary Chiral-Dopant Antiferroelectric Mixtures

DEVEN D. PARGHI[a], JAN P. F. LAGERWALL[b], GERD HEPPKE[a]
[a] Technical University of Berlin, Str. des 17 Juni 135, 10623 Berlin, Germany; [b] Chalmers University of Technology, S-412-96 Göteborg, Sweden

Recent examinations on binary chiral-dopant antiferroelectric liquid crystalline mixtures revealed an unusual switching behaviour. In order to investigate the switching processes that take place in the mixtures, both in the bulk and as influenced by surfaces, further electrooptic and dielectric spectroscopy studies have been carried out on two model binary mixtures in the induced SmA*, SmC* and SmC$_A$* phases. The dielectric spectra feature the different modes typical for these phases, but of varying purity, indicating a more complex phase behaviour than expected. The electrooptic behaviour in the antiferroelectric phase varied from clearly antiferroelectric to near hysteresis-free switching directly between ferroelectric states. We conclude that the phase sequence, and consequently switching behaviour, is a function of both the type of dopant used and of the strength of the surface interactions (cell thickness). In thin cells synclinic (ferroelectric) ordering appears to be favoured.

INTRODUCTION

Liquid crystal devices based on the antiferroelectric smectic C* (SmC$_A$*) phase offer a number of advantages to those based on the nematic phase

(TN- and STN-LCDs) [1]. Several examples of prototype display devices using the SmC_A^* phase (AFLCDs), in the surface-stabilized state [2], have already been realized [3] including examples utilising the effect commonly referred to as "V-shaped switching" [4]. AFLCDs are reported to show wide viewing angles, fast response times, good contrast ratios, and do not suffer from the problems of "image sticking" associated with some other types of LCDs.

Optimising the mixtures for use in any type of LCD is necessary in order to achieve all the possible advantages offered by the device. The technique employed for designing mixtures used in the majority of both prototype, and indeed now commercially-available, surface-stabilized ferroelectric liquid crystal display devices (SSFLCDs) is based on the chiral-dopant concept [5]. In this system a small quantity of a chiral dopant is added to an achiral host mixture possessing suitable mesomorphic and physical properties. This induces a spontaneous polarisation into the mixture, which allows the mixture to be "switched" whilst maintaining the low viscosity typical for an achiral mixture, and does not adversely affect the upper transition temperature of the induced SmC^* phase (if the appropriate quantity of dopant is used).

A number of simple binary mixtures were examined recently in order to test the feasibility of this concept for devices utilising tristate switching [6]. Although these mixtures were found to switch electrooptically at room temperature in aligned test cells, it was uncertain whether the switching was *ferroelectric* (directly between two ferroelectric states) or *antiferroelectric* (switching between the two ferroelectric states via the antiferroelectric state) in character. This was principally due to the absence of a clearly observable antiferroelectric state during the switching process even at applied frequencies lower than 0.1 Hz. The phase was, however, classified as SmC_A^* in the first instance by observation of the characteristic textural defects common to liquid crystals with an anticlinic smectic C phase [7].

In this paper we have set out to study more closely the unusual switching behaviour of two model binary chiral dopant AFLC mixtures by means of electrooptic and dielectric spectroscopy investigations. In addition to investigating the influence of dopant materials, we have also studied the effects of sample thickness and surface influences on the measured physical properties of the mixtures.

EXPERIMENTAL

Since the transition to the SmC_A* phase from the SmC* phase is of interest in purely chiral antiferroelectric materials, a host material, (R/S)-10F1M7 with SmA, SmC and SmC_{alt} phases was selected for these studies [8]. The dopants and their quantities were specifically selected in order to maintain the occurrence of the chiral versions of these phases. In the first mixture (CDMix1) the host material is doped with 15% (by weight) of the standard antiferroelectric material (S)-MHPOBC. The second mixture (CDMix2) contains 10% of a standard non liquid-crystalline ferroelectric dopant.
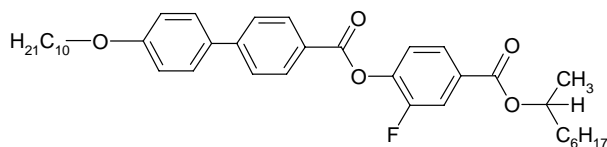

FIGURE 1. Structure of the racemic host material, (R/S)-10F1M7.

The mixture components were weighed together in aluminium pans on a Mettler ME22 balance up to the total weight of 5.00 mg ("100%"). The components were mixed in the isotropic phase (in the pans) on a Wagner & Munz heating bank using a capillary tube sealed at one end.

Transmission vs. applied field plots were recorded on a Gould 1624 oscilloscope using an SMT photomultiplier attached to a WILD M420 microscope. A Keithley 3930A Multifunction Synthesizer connected to a Krohn-Hite 7500 power amplifier was used to generate the applied fields. The test cells (5 µm Linkam, anti-parallel buffing; 10 µm and 2 µm EHC, parallel buffing) were held in a Linkam THM600 hotstage connected to a Linkam TMS90 temperature controller. The cell thickness values are the ones given by the manufacturer, which especially in the EHC case seem to differ somewhat from the actual values. The mixtures were aligned in the cells by application of an AC field (50 - 100 Hz, 100 - 180 V) on cooling slowly from the isotropic phase into the SmA* phase.

The dielectric spectroscopy studies were performed on self-made cells of 4µm thickness with anti-parallel buffed polyimide (Dupont PI2611) and 25µm EHC cells with parallel-buffed polyimide, using the HP4192 dielectric bridge (10Hz - 13 MHz measuring range). The cells

were filled in vacuum in the isotropic or SmA* phase using capillary action. Before starting the measurements they were aligned by applying an AC electric field (10-20 Hz, 10-60V) while heating across the transitions between the different smectic phases. The cells were placed in a Mettler FP80 hot-stage and the temperature was monitored using a PT-100 sensor connected to a thermometer. The entire setup was controlled by a PC running "Labview". The plotted data was fitted to the Cole-Cole equation using "Pro-Fit" for the Macintosh.

RESULTS AND DISCUSSION

Mesomorphic Properties

The phase sequences of the mixtures and the racemic host material are given in Table 1. The transition temperatures for the induced chiral phases of CDMix1 are raised in comparison with the non-chiral phases of the pure host material; this is no doubt due to the miscibility of the phases of the host material with the analogous chiral phases observed at higher temperatures in the antiferroelectric dopant. Although the non-liquid crystalline ferroelectric dopant is partially miscible with the host material the quantity of dopant used in CDMix2 is sufficient to destabilise all of the observed phases, and the transition temperatures are consequently lowered.

TABLE 1. Phase sequence on cooling, as obtained by optical microscopy, of the materials under study.

Mix. / *Host*	SmC_A* / SmC_{alt}	T_c (°C)	SmC */ *SmC*	T_c (°C)	SmA*/ *SmA*	T_c (°C)	Iso
CDMix1	❍	82,6	❍	87,1	❍	116,1	❍
CDMix2	❍	48,4	❍	59,0	❍	101,5	❍
(R/S)-10F1M7	❍	*79,5*	❍	*83,0*	❍	*111,0*	❍

Electrooptic measurements

During initial measurements on CDMix1 we observed an increase, decrease, and increase once again in the value of the observed spontaneous polarisation on cooling from the isotropic liquid [6]. This behaviour,

observed by application of an electric field maintained at a constant value, was not comparable with the behaviour of pure antiferroelectric materials. The cause was postulated as being changes in the threshold voltages required for switching from the antiferroelectric to the ferroelectric state, throughout the SmC_A^* phase. In order to investigate this postulation the values of the DC "after-threshold" fields (the strength of the field at which the material is completely switched to the ferroelectric state) were measured for each mixture in aligned test cells of different thickness and alignment method. The results, together with those of pure (S)-10F1M7 (the chiral analogue of the host material; included as a reference) are shown in Figure 2. For CDMix1 the above postulation does indeed appear to be the case. This is true for all thicknesses of cells used although the DC after-threshold voltages for the 10 μm-thick cell rises above the measurement limits of the equipment. At room temperature the value drops to a measurable size.
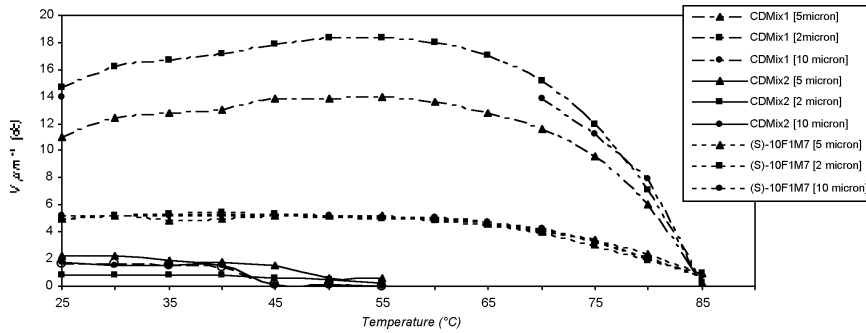

FIGURE 2. DC "after-threshold" voltages for CDMix1, CDMix2 and (S)-10F1M7 (V μm^{-1}). The measurements were taken from the point at which the spontaneous polarisation is observed on cooling from the SmA* phase.

Another interesting feature of the graph is that unlike pure (S)-10F1M7, in which the after-threshold voltages are similar in value regardless of the thickness of the cell, both mixtures show different values in different cells. This suggests that cell thickness has a greater effect on mixtures of this type than on the purely-chiral material.

In order to investigate the switching processes of both mixtures a series of transmission vs. applied voltage curves were measured for all

three types of cells at room temperature. The results are presented in Figures 3 and 4. As with most antiferroelectric materials, increasing the frequency of the applied field increases the degree of ferroelectric switching, and vice versa.

CDMix1 appeared to show only ferroelectric switching from 1Hz down to 10 mHz. Antiferroelectric switching, with a contribution from ferroelectric switching, could only be observed at very low frequencies. Figure 3a shows the unusual switching behaviour of the mixture observed in a 2 μm cell at a frequency of 5 mHz. Close to the "dark" state the transmittance appears to jump to a value higher than the "light" state. This is most probably a birefringence effect; during the switching the direction of the optic axis may change such that it is closer to achieving the $\lambda/2$ condition than in the relaxed state. In the 5 μm-thick cell at the same frequency the switching is almost completely antiferroelectric in character (Figure 3b). A measurement for the 10 μm cell could not be carried out due to the very high field strengths required for switching to the ferroelectric state.
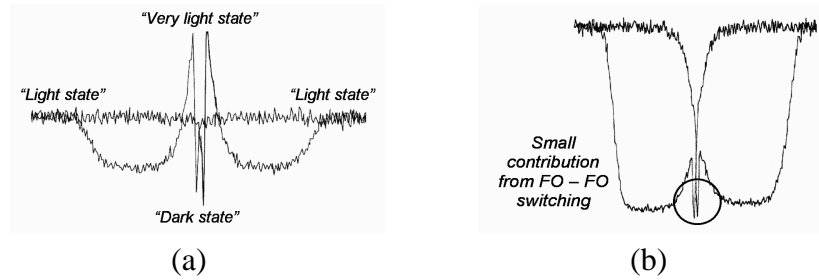

(a)   (b)

FIGURE 3. Switching behaviour in CDMix1. (a) 2μm, 5mHz (150V$_{pp}$), (b) 5μm, 5mHz (85V$_{pp}$)

CDMix2 did not appear to show any antiferroelectric switching in the 2 μm and 5 μm-thick cells even at very low frequencies. Instead we observed almost hysteresis-free switching between ferroelectric states (Figure 4). On increasing the cell gap to 10 μm this switching behaviour was mixed with a component of antiferroelectric switching. Considering that the texture of the mixture on glass slide (under crossed polarisers) identifies the phase as SmC$_A$*, this is a clear indication that the cell surfaces play a major role in determining the structure of the smectic phase.
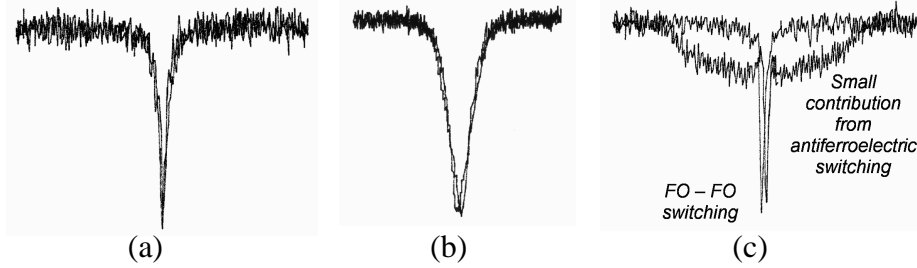
FIGURE 4. Switching behaviour of CDMix2. (a) 2 μm, 5 mHz (36 V$_{pp}$),
(b) 5 μm, 5 mHz (21 V$_{pp}$), 10 μm, 5 mHz (41 V$_{pp}$)

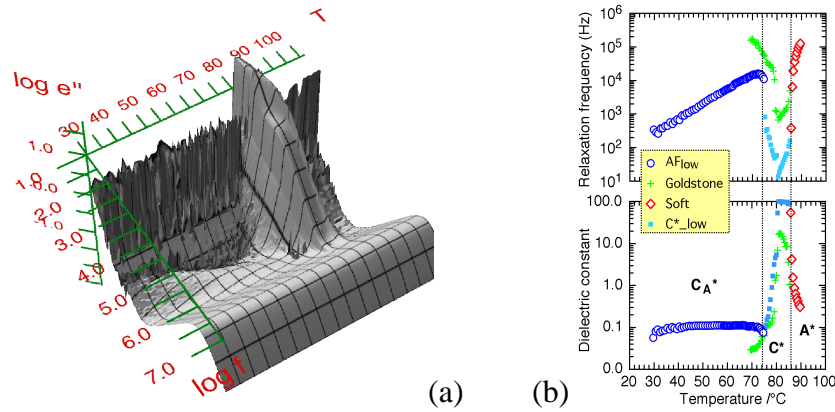

FIGURE 5. (a): Dielectric spectrum of CDMix1 in a 4 μm cell obtained
on cooling. Measuring field: 75 mV/μm (b): Fitted data from
the same measurement. The upper antiferroelectric mode
(AFO$_{high}$) was too weak to be correctly fitted.

Dielectric spectroscopy studies

Dielectric spectroscopy measurements were performed on the two mix-
tures throughout the whole mesophase temperature range. Both showed
the SmA*, SmC* and SmC$_A$* phases, distinguished in the dielectric
spectrum by the soft [9], Goldstone [9] and the two antiferroelectric
modes [10], respectively, but the purity of the phases varied drastically.

The antiferroelectric modes of CDMix1 in a 4 μm cell were weak (Figure 5) and on cooling the Goldstone mode remained for some degrees after the SmC*→SmC$_A$* transition. This suggests that there is some degree of coexistence between SmC* and SmC$_A$* phases below the transition temperature. In the thick cell such behaviour was not observed.

The apparent phase coexistence was much more pronounced in CDMix2, especially in the 4 μm cell. Throughout the entire SmC$_A$* phase the Goldstone mode dominated the dielectric spectrum both on heating (Figure 6) and on cooling. A curiosity is that the soft mode and Goldstone mode are not degenerate at the transition SmC*→SmA*. By applying a DC bias the Goldstone mode could be quenched, revealing the antiferroelectric modes in the SmC$_A$* phase. In the 25 μm cell (Figure 7) there is a range of pure SmC$_A$* on heating from room temperature, but just below 40°C, the Goldstone mode appears and then continually increases in strength up to the complete transition to SmC*. On cooling the phase coexistence continues down to room temperature also in this cell.
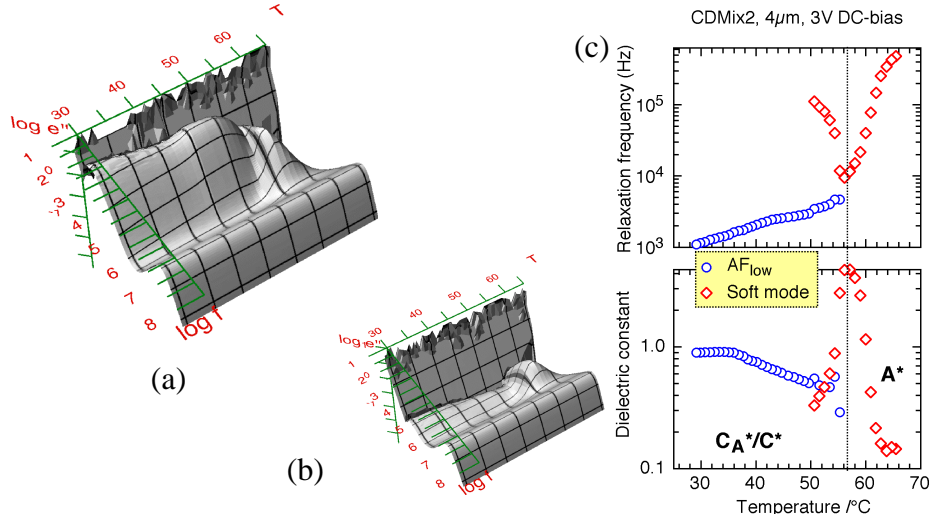

FIGURE 6. (a): Dielectric spectrum of CDMix2 in a 4 μm cell obtained on heating. Measuring field: 75mV/μm. The Goldstone mode is visible throughout the entire SmC$_A$* phase. (c): With a bias field of 3V the Goldstone mode is quenched and the lower antiferroelectric mode is clearly seen. (d): Fitted data corresponding to (c). The upper antiferroelectric mode (AFO$_{high}$) was too weak to be properly fitted.
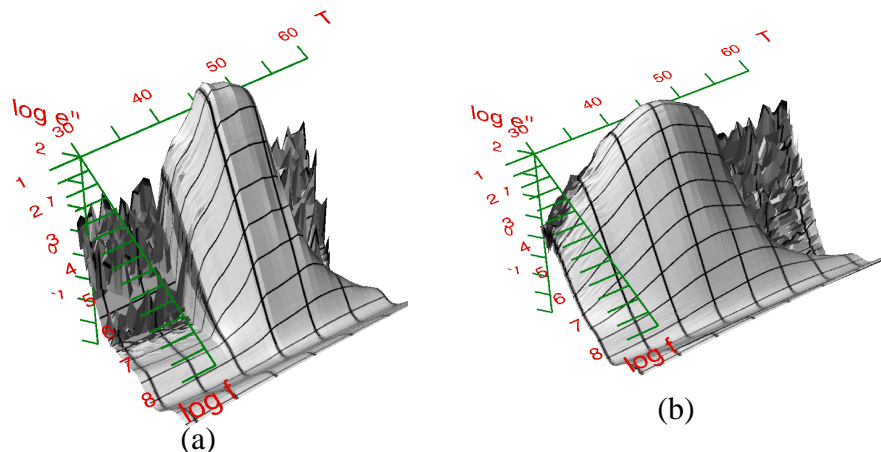
FIGURE 7. Dielectric absorption of CDMix2 in a 25 μm cell. Measuring
field: 20 mV/μm. (a) heating at 1°C/min;
(b) cooling at 1°C/min.

CONCLUSIONS

The conclusions of these observations are that the stability of the SmC_A^*
phase of the doped mixture depends heavily on the type of dopant used,
as well as on the cell gap. With the same host we have obtained mixtures
which show clean SmC^* and SmC_A^* phases separated by a distinct tran-
sition, as well as mixtures where a component of the SmC^* phase pertains
throughout the whole of the SmC_A^* phase. It is evident that strong sur-
face interactions (as seen in thin cells) favour the SmC^* phase, which
suggests that the molecular structure close to the cell surfaces is synclinic
regardless of the bulk phase.

References
[1] A. Fukuda, Y. Takanishi, T. Isozaki, K. Ishikawa, H. Takezoe,
    J. Mater. Chem., **4**, (1994) 997
[2] N. A. Clark, S. T. Lagerwall, Appl. Phys. Lett., **36** (1980), 899

[3] N. Yamamoto, Y. Yamada, K. Mori, K. Nakamura, T. Hagiwara, Y. Suzuki, I. Kanamura, H. Orihara, Y. Ishibashi, Jpn. J. Appl. Phys., **29** (1990) 1757

[4] S. Inui, N. Iimura, T. Suzuki, H. Iwane, K. Miyachi, Y. Takanishi, A. Fukuda, J. Mater. Chem., **6** (1996) 671

[5] T. Geelhaar, Ferroelectrics, **85** (1988) 329

[6] D. D. Parghi, S. M. Kelly, J. W. Goodby, presented at BLCS'99, Durham, UK (1999)

[7] Y. Takanishi, H. Takezoe, A. Fukuda, H. Komura, J. Watanabe, J. Mater. Chem., **2**, (1992) 71

[8] D. D. Parghi, S. M. Kelly, J. W. Goodby, presented at ILCC'98, Strasbourg, France (1998)

[9] F. Gouda, K. Skarp, S. T. Lagerwall, Ferroelectrics, **113**, (1991) pp. 165-206

[10] K. Hiraoka, H. Takezoe, A. Fukuda, Ferroelectrics, **147**, (1993) pp. 13-25