

This article was downloaded by:

On: 26 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

Investigation of flexoelectric properties of a palladium-containing nematic liquid crystal, Azpac, and its mixtures with MBBA

A. G. Petrov^{ab}; A. Th. Ionescu^{ac}; C. Versace^a; N. Scaramuzza^a

^a Dipartimento di Fisica, Università della Calabria and Consorzio INFN, Rende, CS, Italy ^b Institute of Solid State Physics, Bulgarian Academy of Sciences, Sofia, Bulgaria ^c Faculty of Physics, University of Bucharest, Bucharest, Romania

To cite this Article Petrov, A. G. , Ionescu, A. Th. , Versace, C. and Scaramuzza, N.(1995) 'Investigation of flexoelectric properties of a palladium-containing nematic liquid crystal, Azpac, and its mixtures with MBBA', *Liquid Crystals*, 19: 2, 169 – 178

To link to this Article: DOI: 10.1080/02678299508031966

URL: <http://dx.doi.org/10.1080/02678299508031966>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Investigation of flexoelectric properties of a palladium-containing nematic liquid crystal, Azpac, and its mixtures with MBBA

by A. G. PETROV†, A. TH. IONESCU‡, C. VERSACE and N. SCARAMUZZA*

Dipartimento di Fisica, Università della Calabria and Consorzio INFM,
Unità di Cosenza, I-87036 Rende (CS), Italy

(Received 20 July 1994; in final form 1 December 1994; accepted 8 December 1994)

Flexoelectricity of pure Azpac (an HOAB-palladium complex) was studied using planar nematic layers under an in-plane electric field. Longitudinal domains were observed with a period inversely proportional to the applied d.c. electric field. These domains were considered as a first experiment manifestation of the theoretical prediction of R. B. Meyer (1969) and their study has permitted the evaluation of the difference in flexo-coefficients $e_{12} - e_{3x}$. Their appearance can also be followed for the non-complexed HOAB, using instant video-microscopy frames.

Mixtures of Azpac, up to 10 wt%, and MBBA were oriented homeotropically and bend flexoelectric deformations were observed, both in d.c. and in a.c. (1 to 1000 Hz) electric fields normal to the director. The dynamics of director reorientation were studied by the method of flexoelectric light modulation. A system comprising a He-Ne laser and a lock-in amplifier interfaced by a PC was developed. By operating this in a frequency sweep regime, viscoelastic spectra of director dynamics were recorded. These spectra were excited using a linear flexoelectric coupling mechanism. Breaks in the spectra were observed in the range 200 to 600 Hz, indicating a cross-over from bulk to surface dissipation of energy. For the first time, a surface viscosity of $2.6 \times 10^{-8} \text{ J s m}^{-2}$ was determined for MBBA homeotropically anchored on a DMOAP-coated glass surface.

In concentrations at low as 2.5 wt%, Azpac was found to cancel the bend flexo-coefficient of MBBA and at higher concentrations, a steep rise in the flexo-coefficient of the mixture was observed, but with an opposite sign. Thus, the application of Azpac as an effective additive for adjustment of the value and sign of the flexo-coefficient in flexoelectro-optic displays or light modulators could be suggested.

1. Introduction

The Azpac complex, [1] (derived from cyclopalladation of 4,4'-dihexyloxyazoxybenzene (HOAB) with $[(\text{PhCN})_2\text{PdCl}_2]$, followed by halo-bridge cleavage with substituted acetylacetonate salt) is a new example of a nematic metallo-organic material (see figure 1). The unusually asymmetric shape of the molecule, deviating from the classical nematic rod-like shape, suggests that pronounced flexoelectric properties may occur for this material. Indeed, the combination of steric asymmetry, due to the off-axis position of the Pd-containing ring, and the electric asymmetry due to the dipole moment of the N-O group is a prerequisite for dipole flexoelectricity [2, 3], especially

* Author for correspondence.

† On leave from the Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tzarigradsko chaussee, 1784 Sofia, Bulgaria.

‡ On leave from the Faculty of Physics, University of Bucharest, Magurele, P.O. Box MG-11, R-76900 Bucharest, Romania.

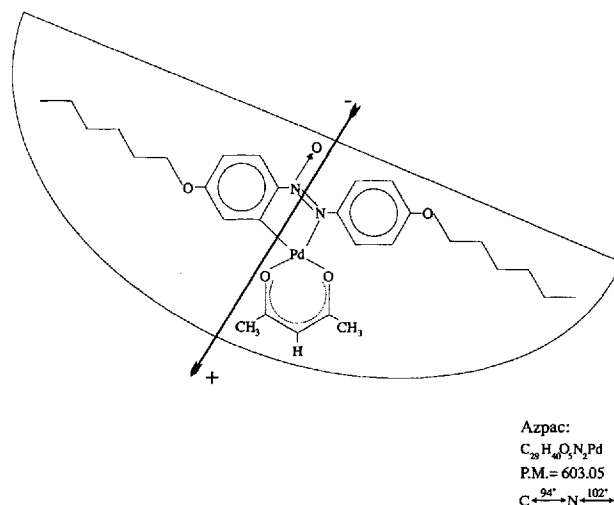


Figure 1. Schematic drawing of Azpac molecule: the banana-like steric asymmetry is emphasized; the physical direction of the molecular dipole is shown by the large arrow. This mutual orientation of the steric and electric asymmetry implies a negative sign of the dipole part of the bend flexoelectric coefficient e_{3x} .

bend flexoelectricity in the present case. First experimental evidence for flexoelectric effects in Azpac was obtained very recently [4], and other material properties of this nematic material, for example, viscoelastic [5] and dielectric [6], have also been investigated.

In this paper further studies of flexoelectricity in thin layers of Azpac in its pure form and in mixtures under the action of in-plane electric fields are reported. Formation of a modulated flexoelectric structure in Azpac has been discovered. Azpac + MBBA mixtures are studied as model systems revealing the effect of Azpac admixture on the flexoelectricity of the host nematic matrix and its performance in a flexoelectro-optic light modulator with d.c., a.c. and combined a.c. + d.c. excitation.

In § 2 of this paper experimental details are presented; results are then reported in § 3 and discussed in § 4, followed by a conclusion in § 5.

2. Experimental

Planar orientation of Azpac was achieved by coating clean glass plates with the ACM-72 polymer surface aligning material (Atomergic Chemetals Corp.) which ensures planar alignment with a small (*c.* 2°) pretilt. A 0.05 wt % solution of ACM-72 in deionized water was prepared; glass plates were immersed in this for 3 min and then removed with a slow vertical motion. The plates were then dried in an oven at 120°C for 20 min and finally buffed unidirectionally with a lens cleaning tissue (Whatman), 20 times. Electrodes were cut from 20 μm Al foil and sandwiched between two ACM-treated plates to act both as electrodes and as spacers. The inter-electrode distance was 0.3–1 mm. The field direction was chosen either parallel or normal to the rubbing direction. Azpac was introduced in its isotropic phase by keeping the cell on a hot plate and planar orientation resulted by slow cooling down to obtain the nematic phase.

Homeotropic orientation of Azpac + MBBA mixtures was achieved by silane coating (DMOAP, Thomson CSF) by dipping the glass plates in a 1 wt % solution of DMOAP in an isopropanol/water mixture (9:1), washing them in water and then curing them at 110°C for 1 h.

Homeotropically oriented cells with horizontal electric field were made from ITO-coated plates with 2 mm etched stripes in the middle of each plate. These stripes were positioned exactly on the top of one another. The distance between the plates was fixed by two pieces of Mylar spacer, typically 75 μm thick, placed either alongside the non-conducting stripes (see figure 2(a)), or across them (see figure 2(b)). The conducting ITO coatings on both plates positioned on the left sides of the non-conducting stripes were electrically connected to each other, as were those on the right side (see figure 2). In this way, two horizontal electrodes were effected, and an in-plane

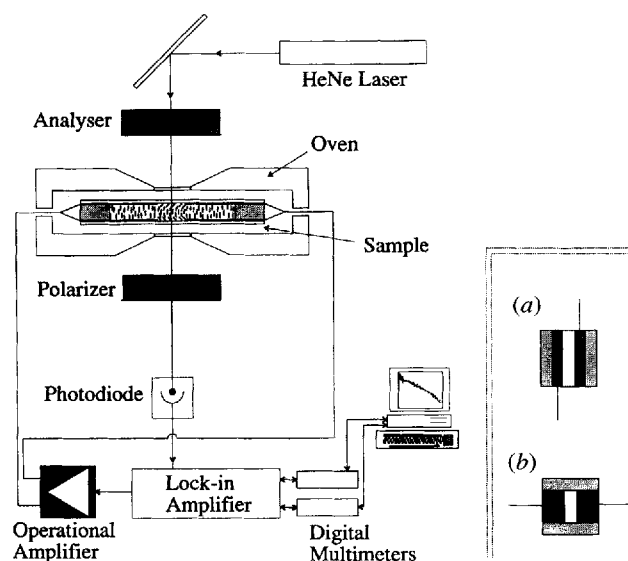


Figure 2. Experimental set-up: 'Flexoelectric Spectrometer' (see text for details). Inset: Sample cells with (a) longitudinal and (b) transverse orientation of the rectangular capillaries: Mylar spacers are shown in light grey and ITO electrodes in dark grey; the etched ITO stripe is shown in white.

electric field was produced in the region of the etched stripes. By placing the edges of the Mylar spacers perpendicular to the non-conducting stripes, a rectangular capillary with open ends was formed (see figure 2(b)) and the nematic layer was left free to flow along the field direction; this was used for determination of the sign of the flexoelectric coefficient (see below).

The present construction of the LC cell (see figure 2) is rather universal. Its four electrodes could be connected two by two to produce either horizontal or purely gradient electric field distribution, and also vertical fields on both sides of the etched stripes. In this manner, various electro-optic effects (linear flexoelectricity [7], gradient flexoelectricity [8] and Fredericksz transition) could be studied in one and the same sample, under identical boundary conditions.

Mixtures of Azpac and MBBA (Eastman Kodak Co.) were prepared by mixing weighted quantities of the two substances and heating the mixture to obtain the isotropic phase. Continuous concentration gradient samples were produced by means of contact preparations where the rectangular capillaries formed by the spacers were oriented parallel to the etched stripes (see figure 2(a)). The capillary was first filled with pure MBBA. Some crystalline Azpac was then placed on one end of the capillary in contact with the MBBA and by slow diffusion, a concentration gradient along the capillary length was established. The local concentration of Azpac was measured based on the fact that it behaves like a dye [9].

Observations of modulated structures (flexoelectric domains) were made using a polarizing microscope, Axioskop Pol (Zeiss), equipped with a Linkam CO 600 heating stage. Video-microscopy was performed using a 3CCD colour camera, TCM 112 (GDS Elettronica), and a Sony U-matic video-cassette recorder VO 5630. Image processing was carried out by a Vidas system (Kontron Bildanalyse GmbH). Video-frames of 512 to 512 pixels were acquired by the frame grabber. Domain periods were measured as a function of the applied voltage by a digital cursor reader with an accuracy of 1 pixel (*c.* 1 μm).

Bend flexoelectric coefficients were measured under d.c. voltage and at room temperature (25°C) by the method described in [7]. Field-induced biaxiality was measured by a 5λ tilting compensator (Zeiss) attached to the Axioskop Pol., using white light (546.1 nm equiv.). The compensation was judged by the restoration of the conoscopic cross.

Flexoelectric coefficients were calculated from the expression for the optical path difference δ versus electric field [7, 10, 11]:

$$\delta = \left(\frac{e_{3x}^*}{K_{33}} \right)^2 n_o \left(1 - \frac{n_o^2}{n_e^2} \right) \frac{d^3}{24} E^2, \quad (1)$$

where K_{33} is the bend elastic constant, e_{3x}^* is an effective bend flexoelectric coefficient standing for the sum $e_{3x} + m_p$, where e_{3x} is the bulk value and m_p is the surface polarization [10, 11] (originating from the biphilic asymmetry of the end substituents of the nematic molecule [3]), n_o and n_e are the ordinary and the extraordinary refractive indices, respectively, d is the layer thickness and $E = U/l$ is the electric field, where U is the voltage and l is the electrode distance.

In contact preparations, the biaxiality was measured at points at different distances from the contact end with Azpac by using the mm scale and vernier of the object holder. A $32 \times$ objective lens was used to reduce the area of the measured spot. Subsequently, the absorption of green light (540 nm) by the MBBA + Azpac in the absence of a field was measured at the same points by a photodiode attached to the camera end of the microscope, and by calibration against the absorption of another homeotropic sample of the same thickness and of known Azpac concentration (5 wt %), the local Azpac concentrations were calculated.

Sign determination of e_{3x}^* was performed by observation of the direction of the flow of LC in the open end samples (see figure 2 (b)) with respect to the electric field [7]. This flow was induced by the space charge due to the curvature and it is expected to be in the field direction at negative e_{3x}^* and opposed to it at a positive value. Observations (by video-taping) of the slow displacement of the nematic-air border were performed with pure and mixed samples by

partially filling the capillary so that the border was positioned within the region of the electric field. Repetitive reversal of the field direction was made in order to confirm the direction of flow.

The dynamics of flexoelectricity of MBBA and MBBA + Azpac mixtures were originally investigated by the method and device for generation and amplification of flexoelectro-optic oscillations of light passing through a homeotropic nematic layer [12, 13]. Recently, flexoelectric oscillations were also generated in pretitled nematic layers and studied by total internal reflection of light from the electrode-nematic interface [14]. Our method essentially consists in simultaneous application of an a.c. electric field $E_1 \cos \omega t$ to the homeotropic samples used for static flexoelectric measurements and a d.c. bias E_0 , creating a static bend deformation over which the surface torque-induced flexo-oscillations are superimposed. The d.c. bias leads to a displacement of the electro-optic system (consisting of two crossed polarizers with the homeotropic layer between them, with the electric field applied at 45° to the polarization plane, see figure 2) from the minimum transmittance to the appearance of a 1st harmonic in the modulated light intensity. The amplitude of the first harmonic is proportional to the 3rd power of the d.c. bias field E_0 and thus strongly amplified [13]:

$$I_\omega = \frac{I_0}{4} \left[\frac{2\pi}{\lambda} \left(1 - \frac{n_o^2}{n_e^2} \right) \frac{n_o}{2} \right]^2 \frac{e_{3x}^{*4} d^4}{6K_{33}^3 \gamma_1^*} \frac{E_0^3}{\omega} E_1 \sin \omega t. \quad (2)$$

This expression is valid in the small angle approximation. Here I_0 is the incident light intensity of wavelength λ , γ_1^* is the rotational viscosity of the nematic, corrected for the back-flow, and the other symbols are as given above. At frequencies above 10 Hz, the 1st harmonic is practically completely dephased with respect to the driving electric field $E_1 \cos \omega t$ (phase shift of 90°, asynchronous regime [13]).

Flexoelectric oscillations originate from oscillating surface flexoelectric torques at the top and bottom layer surfaces [13]. Their penetration depth, ξ , is frequency dependent (this is similar to the thermal wave penetration problem [13]): $\xi = (K_{33}/\omega\gamma_1^*)^{1/2}$. This suggests the opportunity for approaching the viscous properties of the weakly anchored LC surface itself, at higher frequencies when curvature oscillations are localized close enough to the interfaces (see below).

The frequency dependence of the modulation depth of the transmitted light was obtained by means of a system (see figure 2) comprising a 1 mW He-Ne laser (Melles Griot), and a 5208 Two Phase Lock-in Analyser (EG & G, Princeton Applied Research) with computer-driven internal oscillator, interfaced to a PC. A linear frequency sweep for a user-defined range and rate was selected from the PC,

amplified by a dipolar operational power supply/amplifier, Kepco Model 80P 500M, and applied to the sample. The d.c. bias was provided by the same power supply/amplifier. The corresponding amplitude and phase of the 1st harmonic of the transmitted laser light were sampled at each frequency point by two digital 3478A multimeters (Hewlett Packard) from the analogue outputs of the lock-in. Sample temperature was varied by using a brass holder with a Teflon jacket, thermostatted by circulating ethylene glycol from a Haake F3 thermostat. The temperature was measured by a 500 Ω platinum resistor S212PG (Minco). Measurements of the 1st harmonic at fixed frequency as a function of temperature were also possible.

In effect, the system developed by us had the performance of a spectrometer for investigation of director dynamics in the low frequency range (up to a few kHz). Linear coupling to the driving electric field was possible due to the flexoelectric effect. Response versus frequency spectra revealed important information about the bulk and surface viscoelastic properties of the nematic. Such a spectrometer can also be applied to investigate the dynamics of other electro-optic effects.

3. Results

3.1. Modulated structures in pure Azpac and HOAB nematic layers

Observations of modulated domain patterns in Azpac are possible close to its nematic–isotropic transition temperature. They are observed in planar oriented layers, applying a d.c. electric field either parallel (not shown) or perpendicular (see figure 3 (a) and (b)) to the director. In the case of $\mathbf{E} \parallel \mathbf{n}$, the appearance of domains at higher fields is preceded by two waves of orientational change propagating from each of the electrodes on switching on the field. This is probably due to the Freedericksz twist instability of the initial director orientation (the dielectric anisotropy of Azpac is negative [6]). No threshold for domain appearance could be defined. The domain period is substantial at lower voltages (exceeding the layer thickness by several times) and is markedly field-dependent. Measurements of domain period are done by using the digital cursor option of the Vidas system (see Experimental). A characteristic feature of the domain periodicity is the sequence of sharp and diffuse dark stripes, especially clearly visible at lower voltages (see figure 3 (a)). The period was measured between any two sharp stripes, including one diffuse stripe in between, and averaged. In figure 4, the domain period versus inverse field dependence is shown for the two geometries. It is reasonably linear in both cases and the extrapolated linear regression lines pass close to the origin. The difference in the slopes may be due to the slightly lower temperature of

the $\mathbf{E} \parallel \mathbf{n}$ sample (see Discussion). At higher voltages, the domain pattern is distorted by the hydrodynamic flow (more pronounced with $\mathbf{E} \perp \mathbf{n}$), but its appearance is faster than the onset of flow (due to the high viscosity of Azpac [5]), so that the observation of the unperturbed pattern is

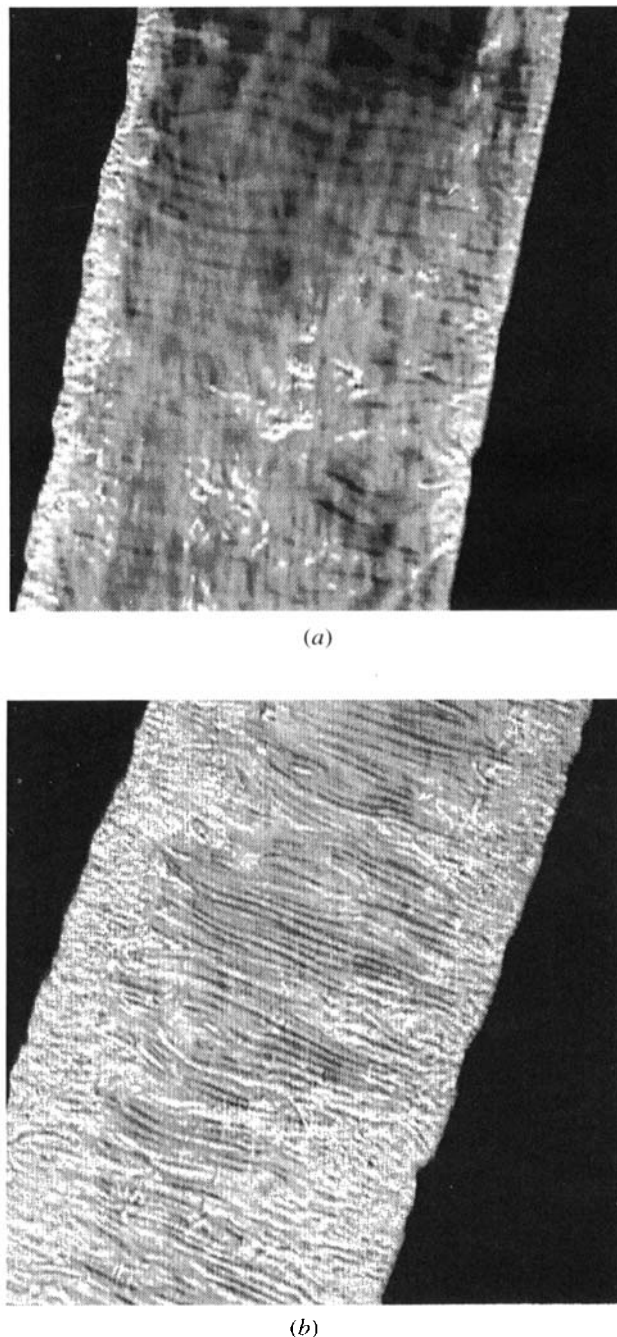


Figure 3. Flexoelectric domains in pure Azpac at different voltages. Layer thickness is 20 μm , electrode distance is 0.3 mm, planar orientation: $\mathbf{E} \perp \mathbf{n}$. Temperature is close to T_{NI} (102°C). Crossed polarizers, parallel to the edges of the photographs. (a) 288 V d.c.; (b) 695 V d.c.

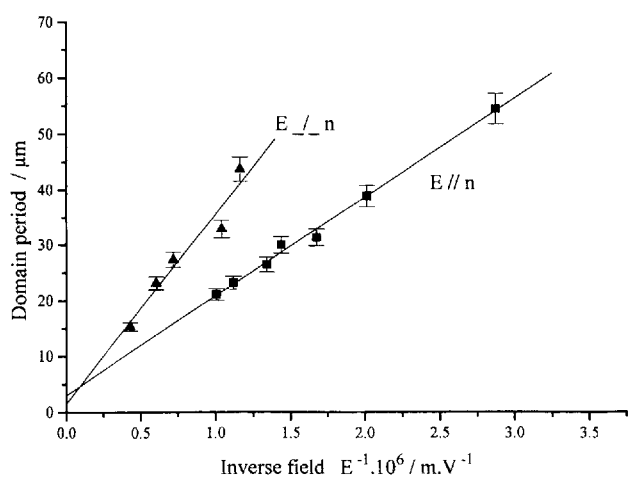


Figure 4. Domain period as a function of the inverse electric field for two cells with different planar orientations: $E \perp n$, electrode distance 0.3 mm (see figure 2) and $E \parallel n$, electrode distance 1 mm. Layer thickness is 20 μm in both samples; temperature is close to T_{N1} (102°C), and slightly lower in that case of $E \perp n$. Lines are linear regressions to the data: $E \perp n$, slope 34.0 ± 4.9 V; $E \parallel n$, slope 17.8 ± 0.6 V.

easily possible on the video-frames just after the field is switched on.

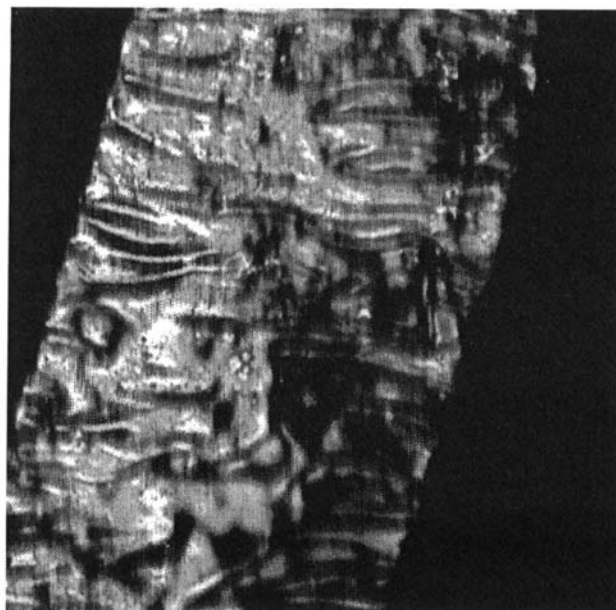
Somewhat surprisingly, a very similar field-dependent domain pattern was detected on the instant video-frames of HOAB as well (see figure 5 (a) and (b)). The viscosity of HOAB is much lower than that of Azpac, and with visual observation, the existence of this domain pattern is completely hidden by the intense hydrodynamic flow.

3.2. Static flexoelectric deformations in homeotropic layers of mixtures

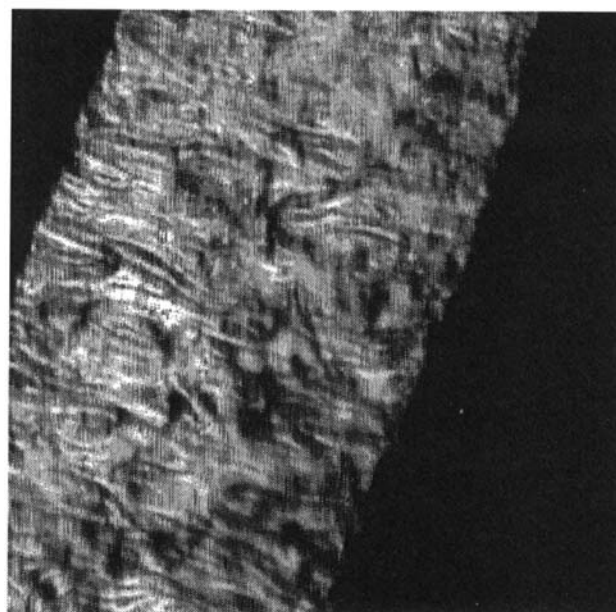
Attempts to orient Azpac homeotropically on DMOAP-treated surfaces failed. Thus, measurements of the bend flexoelectricity of the pure metallo-organic nematic were not possible. Instead, mixtures of this substance with a nematic matrix of known flexoelectric properties were used in an attempt to follow the tendency with increasing concentration. However, mixtures containing Azpac above 10 wt% were also found to be non-orientable homeotropically by DMOAP. Therefore, measurements were limited to below 10 wt%.

On figure 6 (a), (b) and (c), the field-induced biaxiality of homeotropic layers of MBBA and two MBBA + Azpac mixtures are represented. From the average slope for positive and negative voltage in figure 5 (a), taking $n_e = 1.75$, $n_o = 1.54$ and $K_{33} = 7.5 \times 10^{-12}$ N [15], the flexoelectric coefficient $e_{3x}^* = 1.3 \times 10^{-12}$ C m $^{-1}$ for MBBA is calculated, assuming that finite anchoring correction is negligible at this thickness. Comparing this value to the result of Schmidt *et al.* [7]: $e_{3x}^* = 1.5 \times 10^{-12}$ C m $^{-1}$, we note a slight discrepancy,

which may be due to the fact that in [7] homeotropy was achieved by lecithin coating and the anchoring strength on DMOAP in our case may be slightly higher.



(a)

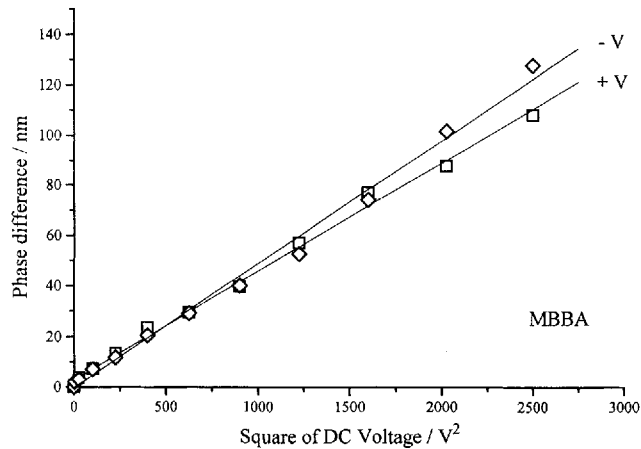


(b)

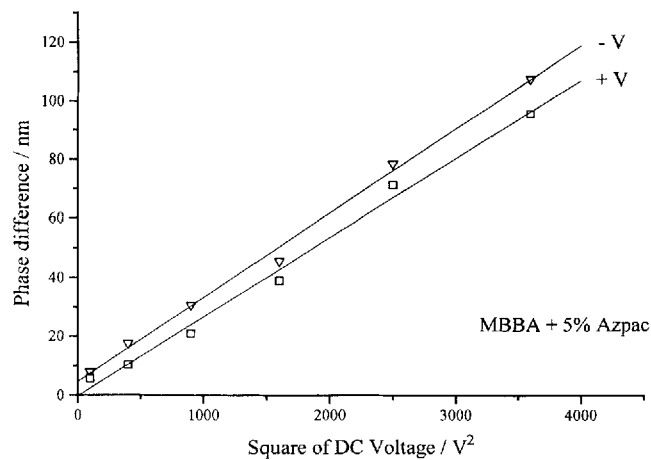
Figure 5. Flexoelectric domains in pure HOAB at different voltages. Layer thickness is 20 μm , electrode distance is 0.335 mm, planar orientation: $E \parallel n$. Temperature is 106°C. Crossed polarizers, parallel to the edges of the photographs. (a) 109 V d.c.; (b) 219 V d.c. Note the disturbance of the domain pattern due to the intense hydrodynamic flow; the period for flow cells is about 6 times larger than the domain period in (a).

Results from the mixtures can be interpreted in terms of an effective e_{3x}^* , if the assumption is made that the refractive indexes and band elasticity are weakly influenced by the Azpac admixture in the low concentration limit. Then, from the average slopes, the following values could be calculated: $|e_{3x}^*| = 1.0 \times 10^{-12} \text{ C m}^{-1}$, i.e. 77 per cent of the MBBA value for 5 wt % of Azpac and $|e_{3x}^*| = 1.84 \times 10^{-12} \text{ C m}^{-1}$, i.e. 141 per cent of the MBBA value for 9 wt % of Azpac. It is clear, that the concentration dependence of the birefringence is not monotonic and in the absence of information about the signs of the flexo-coefficients, their dependence also looks non-monotonic.

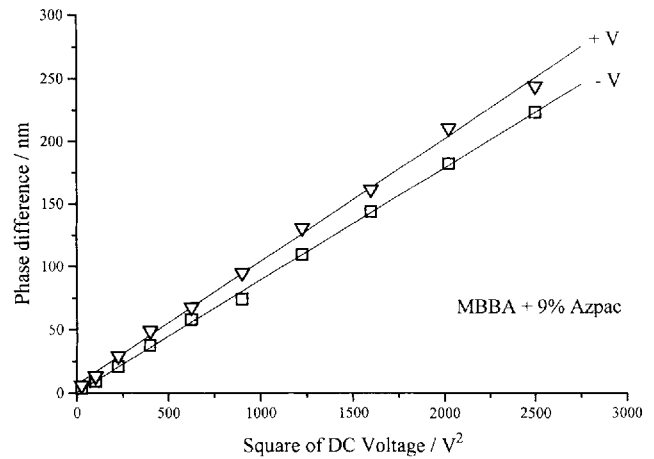
We then proceeded with the measurements of samples with a continuous concentration gradient. The highest concentration in the immediate contact with Azpac crystals achievable in this way was about 7 wt %. It was calculated from the measured absorption of the sample at that point (see above). The most interesting finding was



(a)



(b)



(c)

Figure 6. Flexoelectric bending of homeotropic layers of MBBA and mixtures with Azpac: phase difference versus square of d.c. voltage. Layer thickness is $75 \mu\text{m}$, electrode distance is 2 mm, temperature is 25°C . Lines are linear regressions to the data; + V and - V indicate the two opposite field directions. The slopes are: (a) pure MBBA, + V: $4.3 \times 10^{-2} \text{ nm V}^{-2}$, - V: $4.9 \times 10^{-2} \text{ nm V}^{-2}$ (b) MBBA + 5 wt % Azpac, + V: $2.7 \times 10^{-2} \text{ nm V}^{-2}$, - V: $2.9 \times 10^{-2} \text{ nm V}^{-2}$ (c) MBBA + 9 wt % Azpac, + V: $9.7 \times 10^{-2} \text{ nm V}^{-2}$, - V: $8.9 \times 10^{-2} \text{ nm V}^{-2}$.

that at 2.7 wt % Azpac, the field-induced biaxiality δ was practically absent at all applied voltages. Closer to the Azpac end, it increased again to values surpassing that of pure MBBA at the end of the sample. Relative values of the flexoelectric coefficient are calculated according to

$$\frac{e_{3x}^*(\text{MBBA} + \text{Azpac})}{e_{3x}^*(\text{MBBA})} = \sqrt{\left(\frac{\delta(\text{MBBA} + \text{Azpac})}{\delta(\text{MBBA})}\right)}. \quad (3)$$

Birefringence yields no information about the sign of the flexoelectric coefficients. Therefore, a separate check of the sign was performed with pure MBBA and the 5 wt % Azpac mixture by following the flow direction in open ended samples. In this way, the positive sign of e_{3x}^* for MBBA from [7] was confirmed, while the 5 wt % mixture was found to feature a negative sign. Assuming continuity, the plot in figure 7 was drawn. It is evident from it, that mixtures of about 3 wt % Azpac are practically compensated in terms of bend flexoelectricity, and an almost linear growth of negative e_{3x}^* is observed above that concentration. If the linear regression is extrapolated to 100 per cent of Azpac, a very high value of $e_{3x}^*(\text{Azpac}) = -32.1 \times e_{3x}^*(\text{MBBA})$ would be expected. However, the concentration interval of our observations is rather narrow and a saturation of the linear regression to lower values at higher concentrations is not excluded.

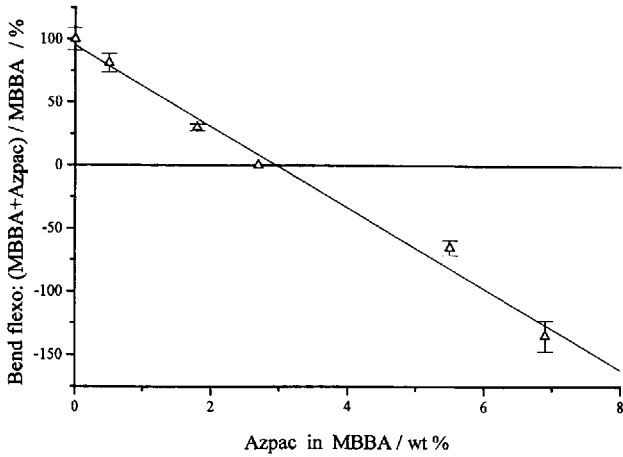


Figure 7. Bend flexoelectric coefficient in a continuous gradient sample versus local Azpac concentration. Layer thickness is $75\ \mu\text{m}$, electrode distance is 2 mm, temperature is 25°C . Applied voltage of 40 V d.c. Locally measured biaxiality is converted in fractions of e_{3x}^* for MBBA. Signs of e_{3x}^* are checked in separate experiments at 0 and 5 wt % Azpac (see text). Slope is -32.1 ± 1.8 .

3.3. Dynamics of flexoelectric oscillations in homeotropic layers

In figure 8, the temperature dependence of the 1st harmonic is displayed for MBBA and two mixtures at identical electric excitation. Increasing the Azpac concentration shifts the transition temperature to higher values. The effect of Azpac of the flexoelectric coefficient and orientational viscosity is evident (cf. equation (2)). The temperature dependence of the 1st harmonic is a combined effect of the variation of e_{3x}^* , K_{33} and γ_1^* .

Figures 9(a), (b) and (c) demonstrate the frequency dependence of the 1st harmonic (spectrum of flexoelectric

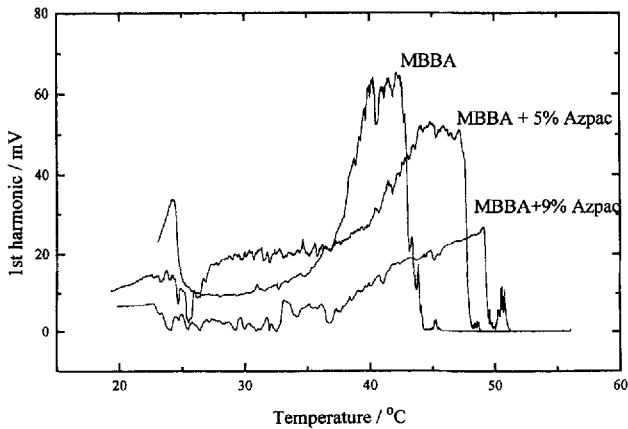
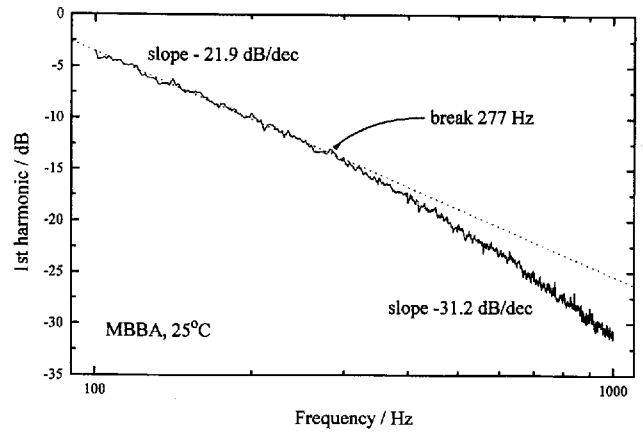
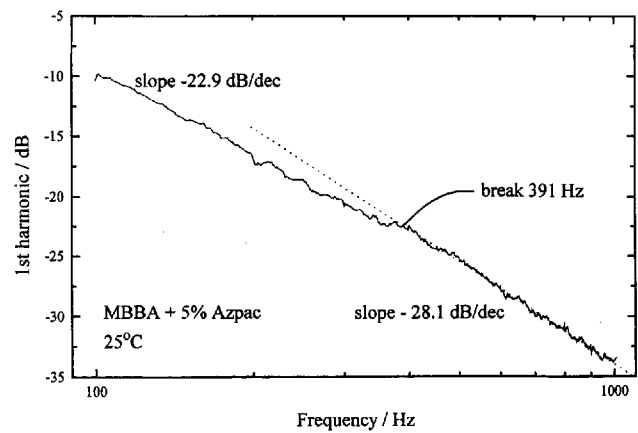


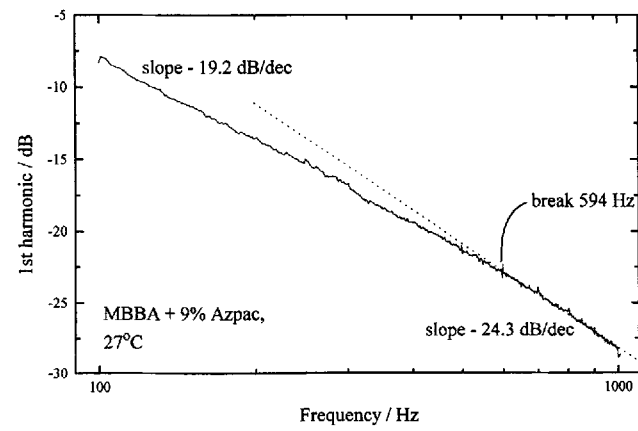
Figure 8. Temperature dependence of 1st harmonic r.m.s. amplitude of flexoelectro-optic oscillations. Layer thickness is $75\ \mu\text{m}$, electrode distance is 2 mm, a.c. voltage is 5 Hz, $30\ \text{V}_{pp}$, d.c. bias is 20 V. The clearing temperatures are 43°C (MBBA), 47°C (MBBA + 5 wt % Azpac) and 49.5°C (MBBA + 9 wt % Azpac).



(a)



(b)



(c)

Figure 9. Frequency dependence of the 1st harmonic at difference Azpac concentrations. Layer thickness is $75\ \mu\text{m}$, electrode distance is 2 mm, a.c. voltage is $30\ \text{V}_{pp}$, d.c. bias is 20 V in (a) and (c) and 40 V in (b). The slopes of the two parts of the spectra and the break frequencies are indicated on the figures. For the sake of clarity only one of the apparent linear fits is shown on each graph.

oscillation) on a log–log scale in the range 100–1000 Hz. Excitation conditions for (a) and (c) are identical, while the d.c. bias is doubled in case (b); thus an amplification factor of 8 is effected (cf. equation (2)) in order to compensate for the decrease of e_{3x}^* in the 5 wt % mixture. In the lower frequency end, the shapes of the spectra closely follow theoretical prediction $\propto \omega^{-1}$, i.e. –20 dB/decade slope on the log–log scale. Breaks are observed at higher frequencies, the slopes tending to –30 dB/decade, i.e. a cross-over to a $\omega^{-1.5}$ shape is taking place. The cross-over frequency increases monotonically from 277 Hz (0 wt %) to 391 Hz (5 wt %) to 594 Hz (9 wt %). This may suggest switching on a new mechanism for energy dissipation, involving surface viscosity (see Discussion).

4. Discussion

The linear dependence of the period of the domains versus inverse electric field is a strong indication of linear electromechanical coupling (flexoelectricity). The first theoretical prediction of a modulated flexoelectric structure with continuous director rotation was made by R. B. Meyer a long time ago [2]. Under the assumption of $e_{1z} = -e_{3x} = e$, the domain period X was obtained as: $X = \pi K/eE$, where K is some average elastic constant of splay and bend. It is easy to generalize this result for arbitrary flexo-coefficients: $X = 2\pi K/|e_{1z} - e_{3x}|E$ (A. G. Petrov, unpublished). Later, the influence of dielectric anisotropy $\Delta\epsilon$ on the domain period was considered [16, 17] and the following expression was obtained (again adjusting it for $e_{1z} \neq -e_{3x}$):

$$X = \frac{2\pi K}{|e_{1z} - e_{3x}|E} \frac{4}{\pi^2} E(k_1)K(k_1), \quad (4)$$

where $E(k_1)$ and $K(k_1)$ are the complete elliptic integrals of the 1st and 2nd kind, and k_1 is given by the implicit equation

$$\frac{E(k_1)}{k_1} = \frac{\pi}{4} \frac{|e_{1z} - e_{3x}|}{\sqrt{(|\Delta\epsilon|\epsilon_0 K)}}, \quad (5)$$

where ϵ_0 is the absolute dielectric permittivity of free space. Solutions of this equation do not depend on the applied field value.

Such a structure was searched for in planar nematic layers and with vertical electric fields, but was never observed. Later, it became clear that it could be realised in an unbounded sample, being otherwise suppressed by anchoring conditions.

We believe that in the present experiments with Azpac (and probably also HOAB), this modulated structure has finally been observed. The peculiarity of our geometry (in-plane electric field) suggests that what we have observed is simply a view from above over the director distribution pattern presented in [2]. The sharp dark lines

in figure 3(a) would then correspond to the regions of splay, while the more diffuse dark stripes between them would be the regions of bend. The initial director orientation, parallel or perpendicular to the field, is unimportant for the appearance of a modulated structure when the director undergoes a continuous rotation. This is in accordance with the observations, and the sample dimensions in the field direction are sufficiently large. The layer thickness is not, but probably the azimuthal anchoring is weak enough to allow the layer to performing as if it is unbounded.

Let us make some numerical calculations. If we introduce the values obtained earlier [4] for Azpac by studying another modulated structure (Bobilev–Pikin's flexo-domains in vertical fields [18]), which is a threshold structure: with $|e_{1z} - e_{3x}| = 3.33 \times 10^{-12} \text{ C m}^{-1}$ and $K = 2 \times 10^{-12} \text{ N}$, the slope of Meyer's domain period versus inverse field would then be 3.8 V. Experimental slopes (see figure 4) are actually larger by factors of 9.0 and 4.7 for the two geometries. An explanation of this discrepancy could be found in the influence of $\Delta\epsilon$: experimental measurements [6] demonstrate that the dielectric anisotropy of Azpac, which is very small near the clearing point (–0.01, cf. [4]), rapidly increases in absolute value on decreasing the temperature, reaching –0.4 within a few tenths of a °C. Such a variation in sample temperature is quite possibly under our experimental conditions. On the other hand, equation (5) has a solution only when $|\Delta\epsilon| \leq \pi^2(e_{1z} - e_{3x})^2/16\epsilon_0 K$, and this limiting value for Azpac is 0.387. When approaching it, the solution of (5) for k_1 tends to 1 and the integral $K(k_1)$ diverges, so that the domain period tends to infinity. Comparing with experiment [6], we see that within a very narrow temperature interval below the clearing point, the critical dielectric anisotropy value of Azpac can even be exceeded. Therefore, the increased slopes of the periods are easily explainable and suggest that the temperature of the $\mathbf{E} \perp \mathbf{n}$ sample was slightly lower than the other. To conclude, the $|e_{1z} - e_{3x}|$ values from the two types of flexo-domains in Azpac seem to agree with each other.

The dielectric anisotropy of HOAB (by comparison with that of PAA) is definitely smaller than for Azpac (less than –0.2), and the temperature conditions for observation of a modulated structure are not so strict. However, the low viscosity of this material has evidently obscured its observation until now, because of hydrodynamic flow.

The results from the observations of static flexoelectric deformations for the MBBA + Azpac mixtures (see figures 5 and 6) can be easily understood in view of the expected negative dipole flexo-coefficient of bend of Azpac (see figure 1). The contribution of Azpac to the effective flexo-coefficient of the mixture, $e_{3x}^* = e_{3x} + m_p$, is most probably to the bulk value e_{3x} and not to the surface polarization m_p , because Azpac, like HOAB has identical

end substituents (see figure 1). Concluding, let us note that to our knowledge this is the first study of flexoelectricity of nematic mixtures.

Results from the dynamics of the flexoelectric oscillations presented by the spectra in figure 9 reveal for the first time the possibility for experimental determination of an important dynamic parameter of the surface, the surface viscosity κ . Extending our calculations from [13], it is easy to see that the contribution of the surface viscosity term $\kappa(\partial\theta/\partial t)$ to the boundary conditions for the flexoelectric curvature oscillations becomes comparable to the bulk viscosity contribution when the excitation frequency exceeds a critical value:

$$\nu_c = \frac{K_{33}\gamma_1}{\pi\kappa^2}. \quad (6)$$

Above this frequency, a cross-over of the frequency dependence of the 1st harmonic of the transmitted light intensity from ω^{-1} to $\omega^{-1.5}$ is predicted, in agreement with the observations. With the experimental value of the critical frequency of MBBA of 277 Hz, and taking $\gamma_1 = 0.077 \text{ J s m}^{-3}$ [15], we calculate from (6):

$$\kappa = 2.6 \times 10^{-8} \text{ J s m}^{-2}$$

for MBBA–DMOAP interface at 25°C which is in good agreement with the data from anchoring breaking experiments with 5CB on a SiO surface [19].

At the cross-over frequency, the penetration depth of the curvature oscillations becomes equal to the ratio of the surface to the bulk viscosity:

$$\xi = \sqrt{\left(\frac{K_{33}}{\omega_c\gamma_1}\right)} = \frac{\kappa}{\sqrt{(2)\gamma_1}}. \quad (7)$$

Making the popular order of magnitude estimation $\kappa \approx \gamma a$, where a is a molecular dimension, we would predict $\xi \approx a$ and the cross-over could hardly be expected to be observable. However, we see that the surface viscosity is actually 2 orders of magnitude larger than the rough order of magnitude estimation which pays no attention to volume–surface dissipative interactions over the plane of anchoring. Therefore, its contribution to the energy dissipation already becomes comparable to the volume contribution below penetration depths of the order of 0.2 μm (which comes from equation (7) at 277 Hz for MBBA).

The shift of the cross-over frequency with increasing Azpac concentration can easily be understood in terms of increased bulk viscosity of the mixtures, evident from the comparison of the absolute values of the modulation depth. There may also be an influence of Azpac on the surface viscosity of the mixture by causing this to decrease, but these two possibilities could not be separated at present.

5. Conclusion

The strong effects of small concentrations of Azpac on the flexoelectricity of mixtures suggest a possible use of this material as an effective additive for adjustment of the value and the sign of the flexo-coefficients in flexoelectro-optic displays or light modulators. Alternatively, compensated flexoelectric mixtures could be prepared, if linear coupling to the electric field is to be avoided in some practical cases. In this way, Azpac could play a role, analogous to the cyanobiphenyls in dielectrically compensated mixtures.

The first experimental observation of surface viscosity demonstrates the effectiveness of the ‘flexoelectric spectroscopy’ method developed by us. Knowledge of this parameter is important for the performance of surface-driven electro-optic devices in the higher frequency range.

The authors are indebted to R. Bartolino, L. M. Blinov and G. Barbero for very useful discussions and to M. Ghedini and D. Pucci for the synthesis of Azpac. This work was supported by BRITE EURAM Project Contract No BRE2-CT94-0614 (grants to A.G.P. and A.Th.I.). A.G.P. is also partially supported by the Bulgarian Fund ‘‘Scientific Studies’’ (Project F-19). A.G.P. and A.Th.I. have the pleasant duty to thank the Unical Liquid Crystal Group for their hospitality.

References

- [1] GHEDINI, M., PUCCI, D., ARMENTANO, S., BARTOLINO, R., VERSACE, C., CIPPARRONE, G., and SCARAMUZZA, N., 16 January 1992, Italian patent No VE92000003.
- [2] MEYER, R. B., 1969, *Phys. Rev. Lett.*, **22**, 918.
- [3] DERZHANSKI, A., and PETROV, A. G., 1982, *Molec. Crystals liq. Crystals*, **89**, 339.
- [4] SCARAMUZZA, N., and PAGNOTTA, M. C., 1994, *Molec. Crystals liq. Crystals*, **239**, 263.
- [5] VERSACE, C., FORMOSO, V., LUCCHETTA, D., PUCCI, D., FERRERO, C., GHEDINI, M., and BARTOLINO, R., 1993, *J. chem. Phys.*, **98**, 8507.
- [6] BEICA, T., ALEXE-IONESCU, A. L., IONESCU, A. TH., MIRALDI, E., PUCCI, D., and RAJTERI, M., 1994, *Molec. Crystals liq. Crystals*, **239**, 203.
- [7] SCHMIDT, D., SCHADT, M., and HELFRICH, W., 1972, *Z. Naturf. (a)*, **27**, 277.
- [8] DOZOV, I., PENCHEV, I., MARTINOT-LAGARDE, PH., and DURAND, G., 1984, *Ferroelectrics Lett.*, **2**, 135.
- [9] VERSACE, C., 1992, Ph.D. Thesis, Università della Calabria.
- [10] PETROV, A. G., and DERZHANSKI, A., 1977, *Molec. Crystals liq. Crystals Lett.*, **41**, 41.
- [11] DERZHANSKI, A., PETROV, A. G., and MITOV, M. D., 1978, *J. Physique*, **39**, 273.
- [12] DERZHANSKI, A., PETROV, A. G., AVRAMOVA, K., and HINOV, H., 25 July 1978, Bulgarian patent No.26915.
- [13] DERZHANSKI, A., and PETROV, A. G., 1979, *Acta Physica Polonica*, **A55**, 747.
- [14] BLINOV, L. M., DURAND, G., and YABLONSKI, S. V., 1992, *J. Phys. II France*, **2**, 1287.

- [15] STEPHEN, M. J., and STRALEY, J. P., 1974, *Rev. Mod. Phys.*, **46**, 617.
- [16] FAN, C., 1971, *Molec. Crystals liq. Crystals*, **13**, 9.
- [17] DMITRIEV, S. G., 1972, *Soviet Phys. JETP*, **34**, 1093.
- [18] BOBYLEV, YU, P., and PIKIN, S. A., 1977, *Soviet Phys. JETP*, **45**, 19.
- [19] GHARBI, A., FEKIH, F. R., and DURAND, G., 1992, *Liq. Crystals*, **12**, 515.