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Measurement of the rotational viscosity of ferroelectric liquid crystals based on a simple dynamical model

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Rotational viscosity and spontaneous polarization are the most important properties of a ferroelectric liquid crystal with regard to its switching time in surface stabilized or a.c. field stabilized displays. Whereas there is an abundant literature about spontaneous polarization, only a few attempts have been made to determine the rotational viscosity. We set up a model for the electric response of a ferroelectric liquid crystal cell on application of an electric field. For the application of a triangular wave voltage we derive a relation between the rotational viscosity, the spontaneous polarization, the tilt angle, the maximum induced polarization current and the electric field strength. Experiments are carried out on several ferroelectric liquid crystals and the derived relation was used to determine the rotational viscosity. The relation between the rotational viscosity and the polarization on the one hand and the optical switching time on the other hand is discussed in some detail.

1. Introduction

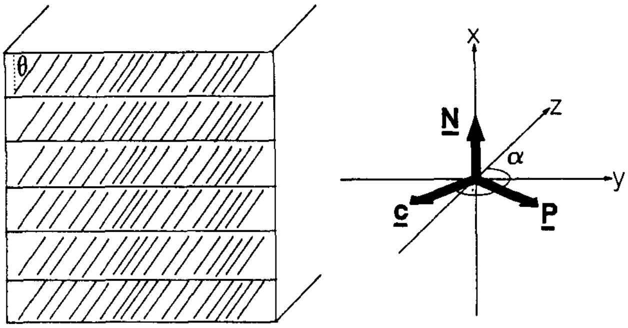
Since the theoretical prediction and experimental verification of ferroelectricity in chiral smectic liquid crystal phases [1] much effort has been devoted to theory [2–12], synthesis [13–30] and experimental investigation of the physical properties [31–50] of ferroelectric liquid crystals. Interest in this subject has increased considerably since it was pointed out in 1980 [51] that such ferroelectric materials can be used in fast electro-optical devices. A large number of articles has now been published [8, 9, 52–70] which focus on the special problems of ferroelectric liquid crystals in thin cells for use as displays. The most striking features of such displays are the possibility of bistability of two optically different states and the fast, field induced transition between these states. The most important physical properties of a ferroelectric liquid crystal with respect to this transition time are its spontaneous polarization, P, and its rotational viscosity, γ. Although there are numerous publications on the polarization of ferroelectric liquid crystals and their mixtures, the literature about the rotational viscosity is scarce [37, 48, 50, 65(a), 71, 72].

One method to determine the spontaneous polarization is to apply a triangular wave voltage to a ferroelectric liquid crystal cell and to measure the induced current [43]. It is obvious that this current contains information not only about the spontaneous polarization but also about the dynamics of the polarization reversal [73]. In order to extract some of this information a simple model is set up for the kinetics of the director on application of an electric field. The model disregards thermal fluctuations and interactions with the walls enclosing the liquid crystal. Furthermore, conditions are worked out under which dielectric and elastic forces can be neglected. The model is used to relate the rotational viscosity, γ, to the applied voltage and the induced current. This relation has been used to determine γ for a number of S_C^* single substances and S_C^* mixtures. The experimental conditions have been chosen so as to satisfy the requirements necessary for the approximations used in the model.

2. Model for the dynamics of the director

Consider a uniformly aligned S_C^* liquid crystal (see figure 1 (a)). Its configuration is characterized by the normal to the smectic layers **N**, the **c** director which is a unit vector parallel to the projection of the long molecular axes on the smectic plane, the polarization vector **P** and the tilt angle θ (see figure 1 (b)). Such a uniform alignment is realized in the bookshelf geometry of a surface stabilized ferroelectric liquid crystal cell [51]. Here the liquid crystal is sandwiched between two ITO coated glass plates which are treated such that the director lies parallel to the glass surfaces. In addition the process of orientation has to ensure that the smectic planes are perpendicular to the cell surfaces. If the cell gap is sufficiently small, the formation of a helix is suppressed even in the bulk of the liquid crystal and we have the desired uniform configuration (see figure 1 (a)). The remaining ambiguity as to whether the director is tilted to the right as depicted in the figure or to the left just reflects the bistability of these two configurations. This degeneracy is removed by applying an electric field $\mathbf{E} = E\mathbf{e}_z$ in the z direction because the polarization vector tends to align parallel to the field. It is this linear coupling of **P** and **E** which leads to the possibility of fast switching between the two stable configurations.

Let us now investigate the dynamics of the polarization reversal in more detail. We assume that the biaxial S_C-structure can approximately be considered as uniaxial with the principal axis parallel to the mean direction of the long molecular axes. As in uniaxial liquid crystals this direction is designated as the director **n**. It was well confirmed in our experiments that both the normal **N** to the smectic layers and the tilt angle θ did not change during the application of an electric field. Hence the only remaining possible motion is a rotation of **n** around **N** which can be described by one variable. For this purpose we choose the angle α between the unit vector in the z direction $\mathbf{e}_z$ and the polarization vector **P**.



(*a*) (*b*)

Figure 1. In a uniformly aligned S_C^* structure (*a*) all molecules are tilted in the same direction with regard to the normal of the smectic layers. Besides the tilt angle θ it is the normal to the smectic layers **N**, the director **c** and the polarization **P** as shown in (*b*) which characterize configuration (*a*). (*b*) shows the angle $\alpha(t)$ between $\mathbf{P}(t)$ and the space fixed z axis.

The external electric field, $\mathbf{E} = E\mathbf{e}_z$, exerts a torque on the liquid crystal which leads to the equation of motion

$$\dot{\mathbf{L}} + \gamma_c \dot{\boldsymbol{\alpha}} + \mathbf{P}_{\text{tot}} \times \mathbf{E} = 0. \tag{1}$$

According to our earlier assumption only the x component of this equation is relevant. $\mathbf{L}$ denotes the angular momentum and $\dot{\mathbf{L}}$ its time derivative. In the following we neglect this last term due to the small moment of inertia of the molecules. The rotational viscosity with respect to rotation about the layer normal $\mathbf{N}$ is denoted by γ_c and $\mathbf{P}_{\text{tot}}$ includes both induced and permanent polarization. We have to distinguish between γ_c and the more fundamental rotational viscosity γ which refers to a uniform rotation about an axis perpendicular to both $\mathbf{n}$ and $\mathbf{P}$. As γ and γ_c transform like components of a tensor, they are related by

$$\gamma = \gamma_c/\sin^2\theta. \tag{2}$$

Here it is assumed that the rotational viscosity for rotation about $\mathbf{n}$ vanishes. The strict validity of equation (1) requires uniform orientation of the liquid crystal at any instant. This point will be examined in more detail later.

The total polarization $\mathbf{P}_{\text{tot}}$ is given by

$$\mathbf{P}_{\text{tot}} = \mathbf{P} + \mathbf{P}_{\text{ind}}, \tag{3}$$

where $\mathbf{P}$ is the ferroelectric polarization and $\mathbf{P}_{\text{ind}}$ is the induced polarization

$$\mathbf{P}_{\text{ind}} = \Delta\varepsilon\, \varepsilon_0 (\mathbf{n} \cdot \mathbf{E})\mathbf{n} + (\varepsilon_\perp - 1)\varepsilon_0 \mathbf{E}. \tag{4}$$

Here $\Delta\varepsilon = \varepsilon_\parallel - \varepsilon_\perp$ is the difference between the dielectric constants measured parallel and perpendicular to the director, respectively. Hence the x component of the torque $\mathbf{P}_{\text{tot}} \times \mathbf{E}$ is given by

$$(\mathbf{P}_{\text{tot}} \times \mathbf{E})\mathbf{e}_x = PE \sin\alpha - \Delta\varepsilon\varepsilon_0 \sin^2\theta\, E^2 \sin\alpha \cos\alpha. \tag{5}$$

For a sufficiently small electric field the second term in equation (5) can be neglected. In order to estimate this field strength we set $\theta = 30°$ which is a rather large value for the tilt and put $\cos\alpha = 1$ which is the most unfavourable value. Then the dielectric term in equation (5) is small as compared with the ferroelectric term provided

$$0{\cdot}22\, |\Delta\varepsilon E/[V\, \mu\text{m}^{-1}]| \ll P/[nC\, \text{cm}^{-2}]. \tag{6}$$

Adjusting the applied voltage to this requirement leads to the dynamical equation

$$\dot{\alpha}(t) = -\frac{P\,E(t)}{\gamma \sin^2\theta} \sin\alpha(t) \tag{7}$$

for $\alpha(t)$.

3. Polarization current on application of a triangular wave voltage

When we apply a voltage U (in the z direction) to a ferroelectric liquid crystal cell we induce the current

$$I = U/R + C\dot{U} + A\,\dot{\mathbf{P}}_{\text{tot}}\mathbf{e}_z, \tag{8}$$

where R is the ohmic resistance of the liquid crystal layer, C is the empty cell capacity and A is the area of the electrode. The use of a triangular wave voltage has the advantage that the ohmic and capacitive contributions to $I(t)$ give straight lines with the slope directly indicating the ohmic resistance. They can therefore be easily subtracted from the total current.

The induced polarization current

$$\mathbf{j} = \dot{\mathbf{P}}_{\mathrm{tot}} \tag{9}$$

has both y and z components but as we only measure the z component, we consider just

$$j = \mathbf{j}\,\mathbf{e}_z = \dot{\mathbf{P}}_{\mathrm{tot}}\mathbf{e}_z, \tag{10}$$

and with $P = |\mathbf{P}|$ we obtain (see equations (3) and (4))

$$j = (-P + 2\Delta\varepsilon\varepsilon_0 \sin^2\theta\, E\cos\alpha)\sin\alpha\cdot\dot{\alpha} + \Delta\varepsilon\varepsilon_0\sin^2\theta\sin^2\alpha\,\dot{E} + (\varepsilon_\perp - 1)\varepsilon_0\dot{E}. \tag{11}$$

The last term only gives a contribution to the straight base lines (and could in principle be used to measure $\varepsilon_\perp$). The second term in the brackets is negligible provided that the condition in equation (6) is fulfilled. Finally we can disregard the third term in equation (11) if

$$\left|\frac{\dot{E}}{E}\right| \ll \frac{P^2}{\gamma\,|\Delta\varepsilon|\,\varepsilon_0\sin^4\theta}. \tag{12}$$

As we apply a triangular wave voltage, equation (12) will certaintly not be fulfilled at any instant. We shall, however, see that equation (12) is valid for those parts of the curve $j(t)$ which we use for the evaluation of γ. A further subtraction of the straight base lines leaves us with the polarization current density

$$j_P = -P\sin\alpha\cdot\dot{\alpha}, \tag{13}$$

and with the aid of equation (7)

$$j_P = P^2E\sin^2\alpha/(\gamma\sin^2\theta). \tag{14}$$

In order to find the time dependence of small j_P we could integrate equation (7) explicitly for a triangularly shaped function $E(t)$ but for the determination of γ we only need the maximum value $j_P(t_m)$ where t_m is given by

$$\left.\frac{dj_P}{dt}\right|_{t_m} = \frac{P^2\sin^2\alpha}{\gamma\sin^2\theta}\left.\left(\dot{E} - 2\frac{PE^2}{\gamma\sin^2\theta}\cos\alpha\right)\right|_{t_m} = 0. \tag{15}$$

This yields the maximum current density

$$j_P^m = \frac{P^2E_m}{\gamma\sin^2\theta}\left[1 - \left(\frac{\gamma\sin^2\theta\,\dot{E}_m}{2PE_m\,E_m}\right)^2\right]. \tag{16}$$

For the experimental conditions which we use, the inequality

$$\left(\frac{\dot{E}_m}{E_m}\right)^2 \ll \left(\frac{2PE_m}{\gamma\sin^2\theta}\right)^2 \tag{17}$$

holds and hence we obtain

$$j_P^m = \frac{P^2E_m}{\gamma\sin^2\theta}. \tag{18}$$

If we account for the area A of the ITO electrodes we can then express γ in terms of the maximum polarization current, $I_P^m = j_P^m \cdot A$, as

$$\gamma = \frac{AP^2 E_m}{I_P^m \sin^2 \theta}. \tag{19}$$

4. Deviations from ideal behaviour

We have already given the conditions in equations (6) and (12) for which dielectric contributions can be disregarded in deriving the relation (19) between the polarization current and the rotational viscosity. Actually the requirement in equation (6) is a little too strong because for the derivation of the maximum current density in equation (18) we have to consider the dynamics of the director in the vicinity of $\cos \alpha = 0$ only. This further reduces the contribution of the neglected dielectric term in equation (5).

The most stringent and most important assumption in our derivation is that the liquid crystal layer is spatially uniform at any instant. On the other hand it is obvious that the ideal homogeneous bookshelf geometry as depicted in figure 1 (*a*) would, ironically, not lead to a field induced polarization reversal at all. This is due to the fact that the electric torque (see equation (5)) vanishes for $\alpha = 0$ or $\alpha = \pi$ which corresponds to a planar alignment of the molecules. Hence a director-component normal to the glass surfaces is needed in order to initiate polarization reversal. The existence of such a component may have various reasons: it may be due to an orientation layer-induced pre-tilt at the surface, to a tendency to form a twisted state [53, 59, 60, 68] or to simply thermal fluctuations. All of these effects will generally be connected with spatial inhomogeneities and lower the peak maximum of the polarization current. This leads to measured γ values which are too large. Furthermore the polarization vector may swing around in opposite directions at different parts of the sample which again may entail increased friction.

In addition spatial inhomogeneities lead to elastic torques which add to the electric torque in equation (5). Our experimental conditions are chosen therefore such that at the polarization current maximum the electric field strength is sufficiently large so as to dominate the elastic forces. This can be checked by applying a d.c. field of this strength. A microscopical observation must then reveal a uniform bookshelf geometry and not a twist state or a helical state.

In summary, both interactions with the walls and bulk properties may lead to spatial inhomogeneity. The influence of the walls can be diminished by using a sufficient cell thickness and the undesired bulk properties can be supressed by a sufficiently strong field. Moreover the frequency of the triangular wave voltage has to be chosen high enough so as to avoid the onset of inhomogeneity near the field reversal points.

5. Experimental section

The experimental set-up which we have used is shown in figure 2. A triangular wave voltage was generated by a frequency generator, amplified and applied to the sample which was sandwiched between two glass plates coated with rubbed polyimide and separated by about 12 μm. The rubbing direction on the two glass surfaces was parallel and an appropriate orientation procedure led (with two exceptions mentioned later) to the desired uniform bookshelf geometry. The voltage was applied by ITO electrodes, with a size of about 0·25 cm^2. The cell was thermostatted in a Mettler hot

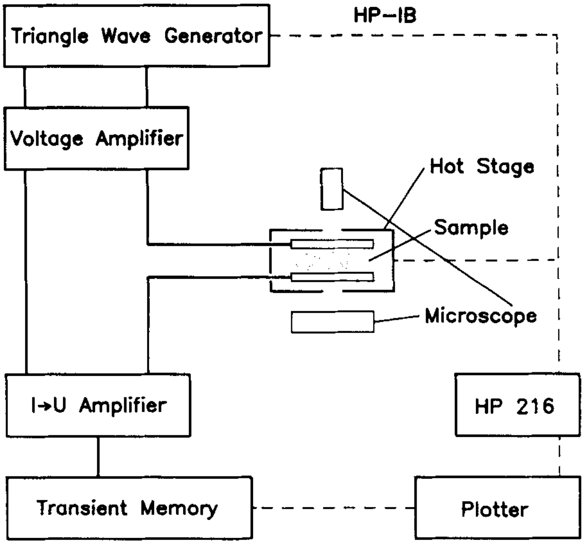


Figure 2. Experimental set-up for the measurement of the spontaneous polarization and the rotational viscosity.

stage. The current induced in the cell was amplified by a current-to-voltage amplifier and stored in a transient memory. From there it was transmitted into a Hewlett-Packard computer and subsequently evaluated. A typical signal is shown in figure 3. All measurements were repeated two times under the same conditions and then repeated with another cell to check for reproducibility and scatter of the data. We found a non-systematic experimental error for γ of up to ± 10 per cent, due mainly

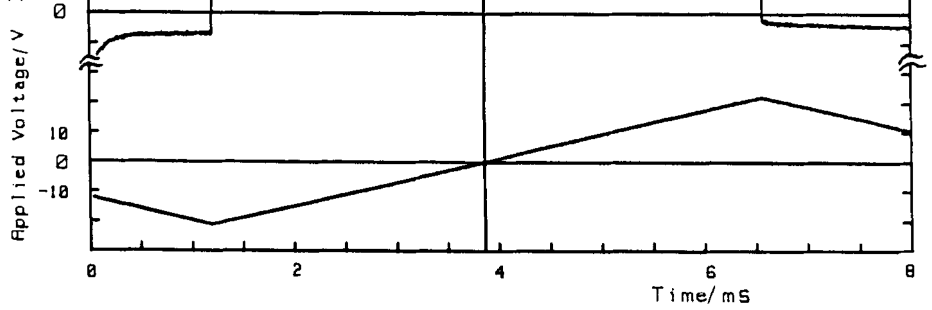


Figure 3. Typical response (upper graph) of the sample circuit on application of a triangular wave voltage (lower graph). Specific figures used for the picture: amplitude and frequency of the applied voltage are 15·4 V r.m.s. and 180 Hz, respectively. The cell gap is 13·2 μm and the ferroelectric liquid crystal is Merck ZLI-3489.

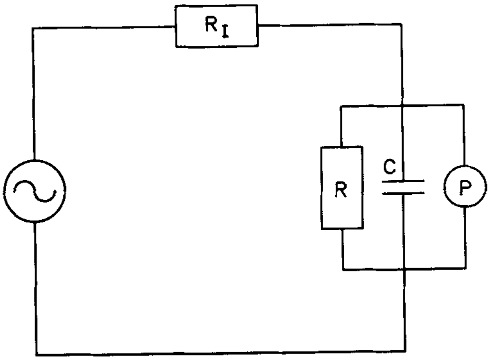


Figure 4. Schematic sketch of the sample circuit as described in the text.

to an error in the measurement of P which according to equation (19) doubles with respect to γ. Both the reproducibility of the electric field E_m, for which the polarization current reached its maximum value I_p^m, and I_p^m itself were reasonably good.

In addition the sample was optically controlled by means of a polarizing microscope. The voltage frequency was lowered from time to time or the power was switched off in order to check if the sample was still uniform.

The frequency and amplitude of the applied voltage were adjusted such that the polarization peak (see figure 3) appeared well after the field reversal of the triangular wave voltage. This ensures that the polarization reversal is determined predominantly by the electric torque and not by the elastic forces. On the other hand we used low enough field amplitudes so that dielectric effects were negligible as compared to the effects due to the spontaneous polarization (*cf.* equation (6)).

To find the limit of time resolution of our set-up we note that the sample circuit can be regarded as a resistance R_I in series with three elements in parallel: a resistance R, a capacity C and a non-linear element with hysteresis due to the spontaneous polarization, P (see figure 4). The resistance R_I is due essentially to the ITO layers, R originates in the ionic conductivity and C in the dielectric properties of the sample. We have $R_I \ll R$ and hence our sample circuit has a characteristic decay time $\tau_d = R_I C$ which is about 1 μs in our case. Of course, the effect of the spontaneous polarization has not been taken into account here. Our result means simply that we can measure characteristic rise times of the polarization current down to about 10 μs, which is sufficient for our purposes.

Both the spontaneous polarization and rotational viscosity were measured in the same experiment. The tilt angle, knowledge of which is necessary for the evaluation of γ, was determined beforehand by optical observation using a low frequency square wave voltage.

The validity of the inequalities in equations (6) and (12) were checked in the vicinity of the polarization current peak and found to be good to within a few per cent.

6. Results

We present measurements on three commercial Merck mixtures ZLI-3234, ZLI-3488 and ZLI-3489 and on two S_C^* single substances. Furthermore we have doped a non-chiral S_C mixture with various chiral components to compare their respective contribution to the rotational viscosity.

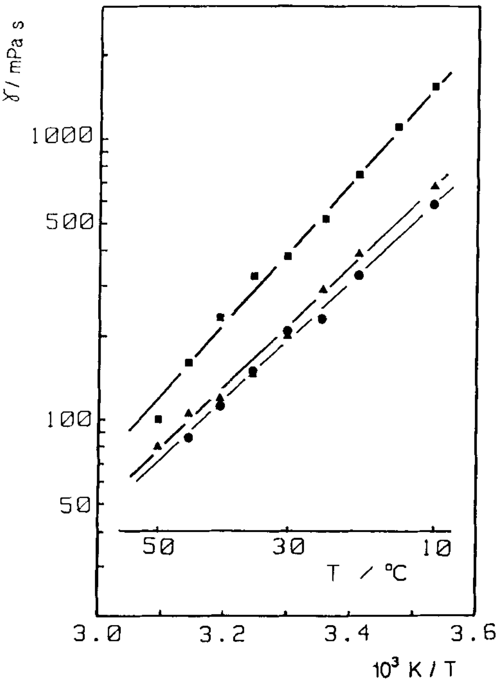
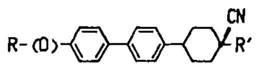


Figure 5. Arrhenius plot for the rotational viscosity of Merck mixtures ZLI-3234 (▲), ZLI-3488 (●) and ZLI-3489 (■).

For all our measurements the temperature dependence could well be modelled by the Arrhenius law

$$\gamma = \gamma_0 \exp (E_A/RT). \tag{20}$$

A least mean square fit was employed and a regression coefficient better than 0·99 was obtained throughout. Figure 5 is an Arrhenius plot of γ for the three commercial mixtures. The main components of these mixtures are homologues of a new class of smectic cyclohexane derivatives with the structure [74, 75]



(I)

These compounds have a good chemical stability, broad S_C phase ranges, a negative dielectric anisotropy and a relatively small optical anisotropy. The larger values of γ for ZLI-3489 are due partly to a larger fraction of chiral components as compared to the other mixtures. Another reason lies in the fact that some of the very same mechanisms which increase P, namely hindrance of intramolecular and molecular rotation, may also give rise to increased γ. From table 1 it can be seen that ZLI-3489 has a much larger spontaneous polarization than the other two mixtures.

It is particularly interesting to compare the rotational viscosity, the spontaneous polarization and the optical switching time, τ_{opt}; this has been done for two temperatures, namely 30°C and 50°C as shown in table 1. For the measurement of τ_{opt} we used the same samples as for the determination of γ and P. They were first adjusted such that the smectic layer normal was parallel to the polarizer and then the stage was rotated by 22·5°. A square wave voltage of 30 $V_{\mathrm{r.m.s.}}$ was applied to the 12 μm thick samples and the transmitted light was detected by a photodiode. The difference in

Table 1. Polarization, rotational viscosity and optical switching time for the commerical Merck mixtures ZLI-3234, ZLI-3488 and ZLI-3489. τ_{opt} is the time between 90 per cent and 10 per cent transmission as explained in the text, measured with a square wave voltage of 2·5 $V_{\text{eff}}/\mu\text{m}$.

	ZLI-3234		ZLI-3488		ZLI-3489	
$T/°\text{C}$	30	50	30	50	30	50
$P/\text{nC cm}^{-2}$	6·8	3·6	7·3	3·5	20·9	12·7
γ/mPas	200	80	210	70	390	100
$\tau_{\text{opt}}/\mu\text{s}$	200	150	190	140	170	80
$\frac{\tau_{\text{opt}}P}{\gamma\sin^2\theta}\Big/\frac{\mu\text{m}}{\text{V}}$	0·39	0·44	0·36	0·58	0·44	0·56

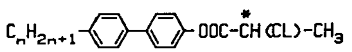
the transmission between bright and dark state was defined as 100 per cent and the time between 90 per cent and 10 per cent was taken as τ_{opt}. For the sake of consistency we took the actually measured values of γ (and P) at 30°C and 50°C rather than the values given by least mean square fits. The tilt angle θ does not play a significant role in our comparison because it does not differ very much from mixture to mixture.

The results in table 1 clearly demonstrate that, to within experimental error, the value of $\tau_{\text{opt}}P/\gamma$ is different for both the mixtures and the two temperatures. This is equivalent to having different proportionality constants in the relation

$$\tau_{\text{opt}} \sim \gamma/P. \tag{21}$$

We do not yet have a clear explanation for the fact that $\tau_{\text{opt}}P/\gamma$ increases with increasing temperature. It might be due to inhomogeneities near the cell surfaces. A definite answer, however, requires more experiments.

We also compared four homologues of the type



(II)

with n = 3, 4, 5 or 6. As the molecules (II) do not exhibit a S_C^* phase we have investigated four identical non-chiral S_C mixtures each doped with 10 per cent weight concentration of one of the homologues (II). The non-chiral S_C mixture contains mainly different homologues of the cyclohexane derivatives (I).

Table 2 shows a reasonable agreement of the values $\tau_{\text{opt}}P/\gamma$ for the various mixtures in view of the unsystematic error of ± 10 per cent in the measured value of γ. Another interesting point is the relatively low value of P for the n = 4 homologue.

Table 2. Polarization, rotational viscosity and optical switching time as defined in the table 1 for a non-chiral S_C test mixture doped with 10 per cent of the n = 3 to n = 6 homologues of molecule (II), respectively.

	$n = 3$		$n = 4$		$n = 5$		$n = 6$	
$T/°\text{C}$	30	50	30	50	30	50	30	50
$P/\text{nC cm}^{-2}$	5·5	2·6	2·9	1·5	4.9	2·4	5·2	2·2
γ/mPas	210	90	200	80	190	80	200	70
$\tau_{\text{opt}}/\mu\text{s}$	340	190	540	250	340	160	340	190
$\frac{\tau_{\text{opt}}P}{\gamma\sin^2\theta}\Big/\frac{\mu\text{m}}{\text{V}}$	0·45	0·45	0·36	0·31	0·44	0·36	0·41	0·40

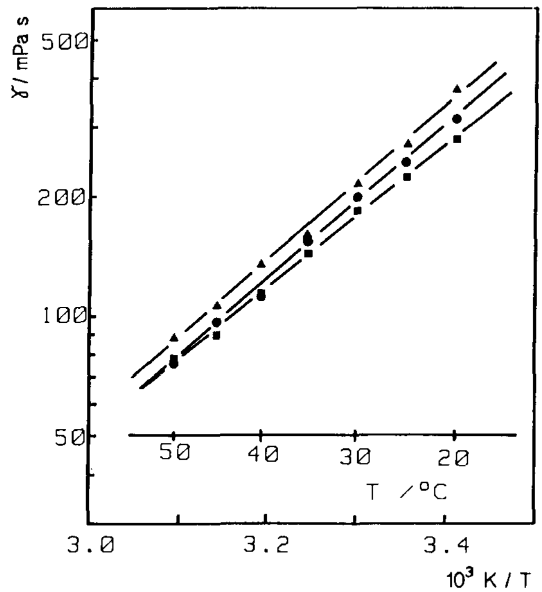
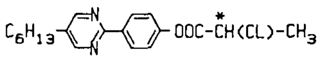


Figure 6. Arrhenius plot for the rotational viscosity of a non-chiral S_C mixture doped with 10 per cent molecules of type (II) (see text) with $n = 3$ (▲), $n = 4$ (●) and $n = 5$ (■).

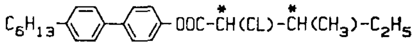
This can be caused only partly by the tilt angle which is about 1°–2° less than that of the other three mixtures. The most important reason is probably a different probability distribution of the $n = 4$ homologue's lateral dipole orientation in the monoclinic cell of the S_C host [69]. On the other hand the variation of γ in this series of homologues is much less pronounced than that of P which suggests that these two properties are not necessarily or exclusively caused by the same molecular mechanism.

The Arrhenius plot of γ for our doped mixtures (see figure 6) confirms a linear temperature dependence of $\ln \gamma$ with an activation energy E_A (*cf.* equation (20)) of about 36 kJ/mole for each of the three homologues.

Additionally we have measured the rotational viscosities of the S_C mixture doped with 10 per cent weight concentration of the chiral molecules:



(III)



(IV)

In figure 7 the temperature dependence of the rotational viscosities of the mixture doped with the $n = 6$ homologue (II) are compared with the mixtures doped with (III) or (IV), respectively. From the results it can be seen that the mixture doped with the biphenyl derivative (II) shows a similar rotational viscosity to the mixture doped with the phenylpyrimidine derivative (III). The phenylpyrimidine doped mixture has a slightly higher spontaneous polarization (6·8 nC/cm² for (III) compared with 5·2 nC/cm² for (II) at 30°C). The properties of the doped mixture change significantly if the chemical structure of the dopant is modified near the chiral centre as in the chiral molecule (IV) where a branched alkyl chain is introduced. This leads to increased values of γ (270 mPas at 30°C) and P (13·3 nC/cm² at 30°C) and to smaller γ/P values compared with mixtures doped with compounds (II) or (III), respectively. On the other hand the activation energy E_A of substance (IV) (43 kJ/mole) seems to be comparable to that of the $n = 6$ homologue of (II) (46 kJ/mole).

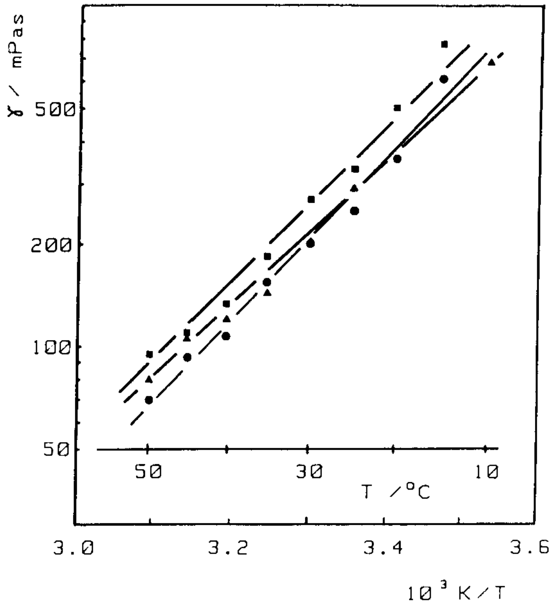


Figure 7. Arrhenius plot for the rotational viscosity of a non-chiral S_C mixture doped with 10 per cent molecules of type (II) with $n = 6$ (●), (III) and (IV). Symbols (▲) and (■) correspond to (III) and (IV), respectively.

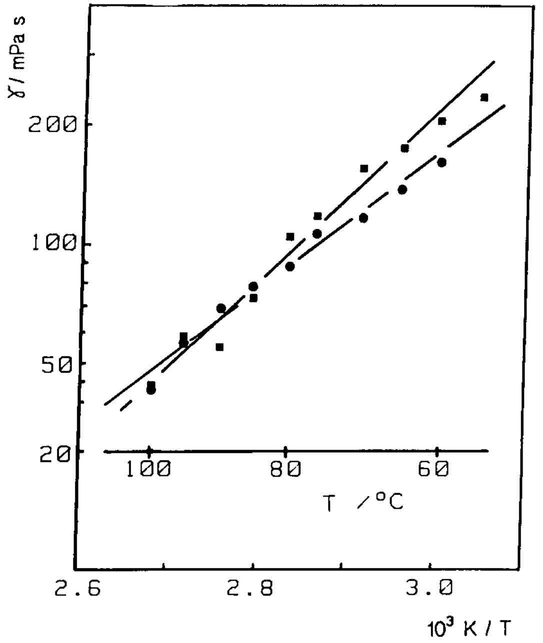
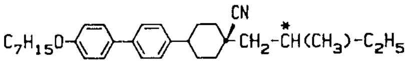


Figure 8. Arrhenius plot for the rotational viscosity of the two S_C^* single substances (V) and (VI). Symbols (●) and (■) correspond to (V) and (VI), respectively.

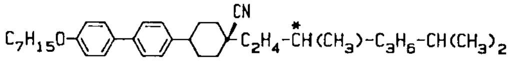
Finally we have investigated the rotational viscosity of the two pure S_C^* single substances



(V)

(C 66°C S_C^* 107°C S_A 112°C Ch 131°C I)

and



(VI)

(C 89°C S_C^* 109°C S_A 118°C I)

Both substances have about the same wide S_C^* range from less than 60°C (supercooled) to more than 105°C. Whereas the spontaneous polarization of the second substance is about three times larger than that of the first, the rotational viscosity does not differ significantly (see figure 8). This again supports the view that γ and P may be caused by different molecular mechanisms.

We must say, however, that we did not succeed in obtaining a uniform orientation in the S_C^* phase of (V) and (VI), but rather found a striped pattern probably due to broken smectic layers. From our earlier experience with mixtures which could be oriented at will uniformly or with stripes we can conclude that the actual values of γ are probably lower than those which we have measured.

7. Discussion

First we compare our way to determine γ with the simple use of the formula $\gamma_{\text{eff}} = \tau_{\text{opt}} PE$ where τ_{opt} is the optical switching time. This formula can be obtained by solving equation (7) for a constant electric field. This yields

$$\tan\frac{\alpha}{2} = \tan\frac{\alpha_0}{2}\exp\left[-\frac{EP}{\gamma\sin^2\theta}(t-t_0)\right],$$

with $\alpha_0 = \alpha(t_0)$. Identifying the characteristic response time

$$\tau = \gamma\sin^2\theta/EP,$$

with τ_{opt} and $\gamma\sin^2\theta$ with γ_{eff} we obtain the relation $\gamma_{\text{eff}} = \tau_{\text{opt}} PE$.

We have to be careful, however, in identifying the response time of α with the optical switching time τ_{opt}. This is due to the following reasons:

The optical transmission is a complicated function of α and depends on both the refractive index of the ordinary and the extraordinary ray;

for white light the optical response also depends on the spectral characteristics of illumination and the photodetector;

the optical transmission is very sensitive with regard to non-uniformities of the sample along the light beam which may, in particular, occur near the walls.

The last point is of particular importance and interest. We carried out a number of experiments which demonstrate this phenomenon very nicely. The optical transmission curve on application of a square wave voltage almost always reveals a more or less pronounced asymmetry of the two switching processes on changing the field polarity from '+' to '−' and vice versa. This asymmetry can be made more pronounced by using a triangular wave voltage. That this asymmetry does not originate in an asymmetry of the physical switching process can easily be demonstrated by turning

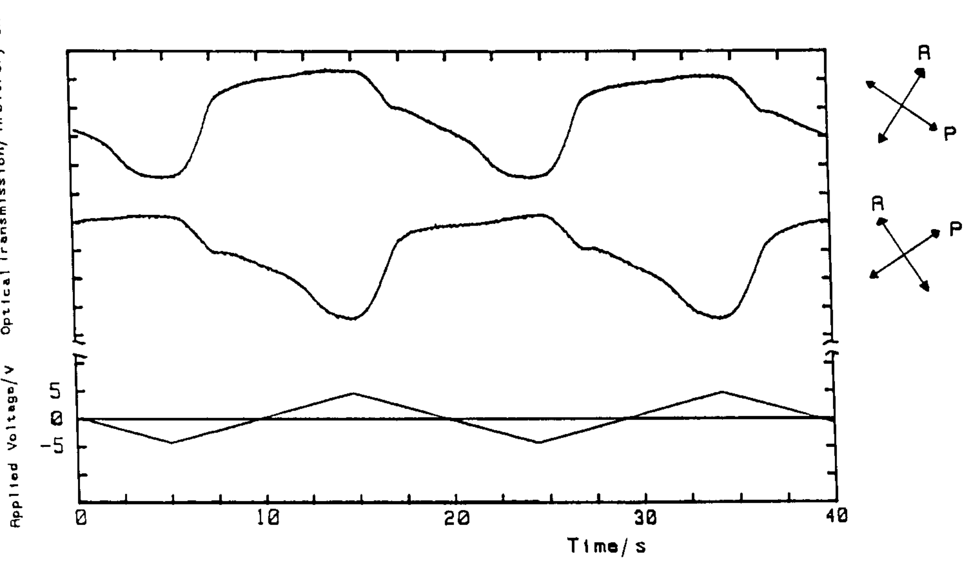


Figure 9. Optical transmission of the sample between crossed polarizers (upper graphs) on application of a low frequency triangular wave voltage (lower graph). In the upper graphs the sample stage is turned such that the layer normal **N** and the direction of the analyser make an angle of $-22{\cdot}5°$ or $+22{\cdot}5°$ as indicated (P = polarizer, A = analyser). Specific figures used for the picture: amplitude and frequency of the applied voltage are $7\,V_{r.m.s.}$ and 0·05 Hz, respectively. The cell gap is $13{\cdot}2\,\mu m$ and the ferroelectric liquid crystal is Merck ZLI-3489.

the sample stage by 45°. The new optical transmission is not the inverse of the previous one but just the previous one shifted by half a period with respect to the applied voltage (see figure 9). Hence both switching processes are totally equivalent and it is the mutual interaction of the polarization direction of the probing light beam and the inhomogenous intermediate cell configuration which is responsible for the asymmetric response.

As the physical switching was found to be symmetric this was, of course, also true for the shape of the polarization peak (see figure 3) as electric response on the rising and falling branch of the applied triangular wave. Hence the evaluation of the polarization peak is a much less ambiguous tool for determining the rotational viscosity than the optical switching time.

Though the optical response of the cell clearly indicates inhomogeneous transition states, which are more or less distorted forms of a so-called twisted state [53, 59, 60, 68], we think that under our experimental conditions these inhomogeneities are kept to a minimum and confined to thin surface layers.

In contrast to our experiments described previously, the optical switching time is predominantly determined in very thin cells with a non-negligible influence of the walls. This is reasonable because practical displays for applications will be very thin and the performance of a display therefore comprises both bulk and cell properties. But, of course, these are unfavourable conditions for the determination of a pure bulk property such as γ.

Finally τ_{opt} is influenced by the whole switching process including its crucial onset, whereas our method to determine γ relies only on the characteristics of the fully developed transition. We have also checked our results for γ by solving equation (7) explicitly and correlating γ with the half width of the polarization peak. Within experimental error the results were the same.

A comparison of γ for our S_C^* substances with the rotational viscosity of nematic liquid crystals [76–81] shows that they do not differ very much but are of the same order. Typical values for broad range ferroelectric liquid crystal mixtures like Merck ZLI-3234 and ZLI-3488 are 200 mPas at room temperature.

With regard to the temperature dependence of γ we could, of course, try a more sophisticated ansatz [78] than our simple Arrhenius law (*cf.* equation (20)). Unfortunately the estimated errors in our measurement do not admit such an attempt. Yet, the appearance of an order parameter in the ansatz is likely to be superfluous in our cases. We did not see any dramatic change in γ on approaching the S_A phase which was above the S_C^* phases for all of our materials. The activation energy E_A ranged from 35 kJ/mole to 50 kJ/mole for the mixtures we investigated. This is slightly higher than the values found for nematic liquid crystals [81].

Finally we note that our results seem to indicate that for the sake of short switching times small values of γ and P are better than large values of γ and P which lead to the same ratio γ/P. This might be due to a tighter coupling to the cell surfaces for large P. This could be one more reason [70] to look for substances with small γ rather than with large P provided that γ/P has about the same value.

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