CHAPTER IV

Determination of Rotational Viscosity in the Smectic C* and Smectic A Phases

4.1 Introduction

Ferroelectric liquid crystals\(^1\) (FLC) have attracted attention owing to their fast electrooptic switching properties, two or three orders of magnitude faster than those of nematic liquid crystals.\(^2\) Thus for certain applications which require fast electrooptic switching characteristics FLCs are extremely useful. One of the important material properties which controls the speed of this switching is the rotational viscosity (\(\gamma_\phi\)) associated with the motion around the smectic C cone.\(^3\)

Several methods\(^4\)\(^−\)\(^10\) have been developed to determine \(\gamma_\phi\). However a detailed comparison of the values obtained by the different techniques does not seem to have been made. Moreover, there are hardly any systematic studies\(^11\)\(^,\)\(^12\) as a function of the alkyl chain length of the molecule. Keeping this in view we have measured the rotational viscosity by different techniques. The results show that under proper experimental conditions, all the methods give the same value of rotational viscosity within the experimental errors. Measurements made on different members of a
homologous series show a systematic variation with changing alkyl chain length. We have also measured the soft mode rotational viscosity\textsuperscript{9,13} $\gamma_s$ by dielectric methods.

The scheme of presentation in this chapter is as follows. First, a brief description of the concept of rotational viscosity of nematic liquid crystals is given, followed by the origin of different rotational viscosities of the ferroelectric smectic C* phase. The various methods employed for the determination of rotational viscosities are then described in detail and the experimental set up used in different cases are explained.

A comparison between the values obtained by the different methods is given. Results of the effect of alkyl chain length on the magnitude and temperature variation of $\gamma_\phi$ are presented. Finally the thermal variation of the soft mode viscosity $\gamma_s$ in the A phase is discussed.

### 4.2 Rotational viscosity in the smectic C* phase

Consider first a nematic liquid crystal in which the director is rotating by the application of an electric or magnetic field rotating about Y-axis. The resistance of the system to such a rotation can be described by the torque equation\textsuperscript{14}

$$\Gamma^n = -\gamma \frac{d\phi}{dt}$$  \hspace{1cm} (4.1)

where $\Gamma^n$ is the torque required to maintain an angular velocity $d\phi/dt$ and $\gamma$ is the associated rotational viscosity coefficient. $\phi$ is the angle the director makes with the initial director position as shown in Fig. 4.1.

The problem is more complicated in the smectic phase due to the presence of layering. But for the type of viscosities that we are interested in, a much simpler approach has been taken and a theory has been developed on the lines of the nematic viscosity coefficients. For this the major assumption that is made is that the
Fig. 4.1. Director re-orientation in the nematic phase under the influence of a field.

Fig. 4.2. Definition of rotational viscosity coefficients in the smectic C* phase.
response of the system is purely confined to director rotation without any translational motion.

To define the rotational viscosity coefficients in smectic C* phase consider Fig. 4.2, where n is the director, 0 the tilt angle, c the in-plane smectic C director, φ its phase and xyz are the rectangular coordinates.

Just like in the nematic case, the viscous torque is given by

\[ \Gamma = -\gamma \frac{d\phi}{dt} \]  

(4.2)

where \( \gamma \) is a general viscosity coefficient. From the symmetry of the smectic C* phase it is clear that one of the principal axes of \( \gamma \) must be in the layer plane and perpendicular to the tilt direction. The corresponding torque is denoted by \( \Gamma_\theta \) and the viscosity is \( \gamma_\theta \). \( \gamma_\theta \) is the viscosity associated with the change in the magnitude of 0, and describes the tilt amplitude fluctuations. The transition between A and C* phases is second order or at most weakly first order. As such close to the transition a tilt fluctuation mode can be observed in the A phase. This mode softens on approaching the transition point. Therefore \( \gamma_\theta \) is called the soft mode viscosity (\( \gamma_s \)).

The second principal axis of \( \gamma \) is parallel to the director. This mode corresponds to the rotation of the molecule about its long molecular axis and the associated viscosity value is very small. The remaining principal axis must be in the tilt plane and perpendicular to the director n and the polarization P. The corresponding viscosity is found to be similar to the nematic rotational viscosity and is denoted by \( \gamma_G \). In the case of the C* phase the director n rotation is damped by a viscous force which is the z-component of the viscous torque acting on the director n. One can obtain an expression for this torque and hence for \( \gamma_G \) by considering eqn.(4.2), i.e.,
\[ \Gamma^G = -\gamma_G \frac{\partial \phi}{\partial t} = -\gamma_G \mathbf{n} \frac{\partial \mathbf{n}}{\partial t} = -\mathbf{n} \gamma_G \dot{\mathbf{n}} \]

To find the value of \( \dot{\mathbf{n}} \) consider the components of \( \mathbf{n} \) along x, y and z axes.

\[
\begin{align*}
    n_x &= n \sin \theta \cos \phi \quad \text{therefore } \dot{n}_x = -n \dot{\phi} \sin \theta \sin \phi \\
    n_y &= n \sin \theta \sin \phi, \quad \dot{n}_y = n \dot{\phi} \sin \theta \cos \phi \\
    n_z &= n \cos \theta, \quad \dot{n}_z = 0
\end{align*}
\]

Therefore \( \dot{\mathbf{n}} = n \dot{\phi} \sin \theta \)

and

\[ \Gamma^G = -\gamma_G \mathbf{n} \cdot \mathbf{n} \dot{\phi} \sin \theta = -\gamma_G \dot{\phi} \sin \theta \quad (4.3) \]

The z component of this torque is \( \Gamma^G_z = \Gamma^G \times \mathbf{0}, \text{ i.e.,} \)

\[ \Gamma^G_z = -\gamma_G \sin \theta \times \dot{\phi} \times \sin \theta = -\gamma_G \sin^2 \theta \dot{\phi} \quad (4.4) \]

Usually one introduces another viscous torque \( \Gamma_c \) for the rotation of the c-director about the layer normal, i.e., z-axis (see Fig. 4.2). The corresponding viscosity is \( \gamma_\phi \) associated with the rotation of c-director about z-axis which is similar to the rotation of the director \( \mathbf{n} \) about the layer normal within the smectic cone. One can obtain an expression for \( \gamma_\phi \) by considering the components of c-director and using the torque equation as

\[ \Gamma_c^C = -\gamma_\phi \mathbf{c} \cdot \dot{\mathbf{c}} = -\gamma_\phi \dot{\phi} \quad (4.5) \]

Comparing Eqs. (4.4) and (4.5)

\[ \gamma_\phi = \gamma_G \sin^2 \theta \quad (4.6) \]
Though $\gamma_\phi$ is the viscosity associated with the rotation of the director $\mathbf{n}$ about the layer normal, but it has been argued\textsuperscript{10} that $\gamma_G$ is the more fundamental rotational viscosity as it defines the rotation of $\mathbf{n}$ about an axis perpendicular to both $\mathbf{n}$ and $\mathbf{P}_r$ lying in the tilt plane. In contrast $\gamma_\phi$ is a derived quantity composed of $\gamma_G$ and $\theta$. Thus the temperature dependence of $\gamma_\phi$ not only involves the temperature dependence of $\gamma_G$ but also the temperature variation of $\theta$. Further if one wants to compare $P_s$ and rotational viscosity, it is $\gamma_G$ which has to be considered and not $\gamma_\phi$, as $P_s$ and $\gamma_\phi$ comparison might include a mutual relation between $P_s$ and $\theta$.

As $\gamma_G$ is related with the rotation of $\mathbf{n}$ about the layer normal, it is also called as the Goldstone mode rotational viscosity (in analogy with the symmetry recovering Goldstone mode studied in dielectrics, Chapter III). A pictorial representation of rotational viscosities in nematic, SmA and SmC*, is given in Fig.4.3.

Rotational viscosity in smectic C* phase is measured by methods based on mechanical,\textsuperscript{15} pyroelectric\textsuperscript{5,16} and electrical\textsuperscript{6-10} techniques. The mechanical methods involve disturbance of the helix in the smectic C* phase by an alternating shear or Poisseuille flow which gives information on the viscoelastic coefficients. However, these methods are not commonly used because of the complicated experimental set up. The pyroelectric method has been successfully employed to determine both $\gamma_s$ and $\gamma_\phi$. In this method using a short laser pulse the liquid crystal layer is heated; due to this heating the director tilt changes and thus the $P_s$ reorients giving rise to an induced pyroelectric current. By studying this transient current decay, $\gamma_s$ value can be obtained. This technique also needs a sophisticated set up. In the electrical method the rotational viscosities can be determined either (a) by studying the current\textsuperscript{6-8} or optical\textsuperscript{4} response to an applied alternating electric field or (b) by dielectric\textsuperscript{9,10} measurements. We have employed the electrical method and used
Fig. 4.3. The single rotational viscosity in the nematic and smectic A phase will be split into two in the smectic C phase, associated with motion on the cone and tilt-angle variations, respectively. (From K. Skarp, Ref. 3).
technique (a) for the measurement of $\gamma_\phi$ and technique (b) for determining $\gamma_s$. The principles involved and the experimental set up are described in detail below.

4.3 Electrical methods of measuring $\gamma_\phi$

In this method $\gamma_\phi$ is usually determined in thin samples by applying an oscillating electric field and either measuring the time required for an optical transmittance change - the optical response method or by measuring the current induced due to reversal of the polarisation - the field reversal method. Usually optical transmission method is done using a square wave, whereas in the field reversal method one can employ a square wave or a triangular wave or a sine wave. Depending on the type of the input wave there are different field reversal methods for measuring $\gamma_\phi$. All these methods are described in the following.

4.3.1 Optical response method

Here a low frequency square wave of sufficiently high amplitude is applied to a homogeneously aligned smectic C* sample and the temporal variation of the transmitted part of an incident polarised light is used as a measure for the calculation of the response time $\tau$, and $\gamma_\phi$ is calculated using an empirical formula $\gamma_\phi = \tau P_s E$, where $P_s$ is the spontaneous polarisation, $E$ is the applied electric field.

To find $\tau$ consider an aligned smectic C* sample. Let all the dipoles be in the up state when the applied voltage is $+V$ at any instant of time. When the direction of the applied voltage changes from $+V$ to $-V$, the dipoles will rotate by an angle $2\theta$ and the dipoles will align in the down state. Because of the viscosity a definite time is needed for the dipoles to orient from $+P_s$ to $-P_s$ and this time is called the switching time $\tau$. The optical switching time $\tau$ is defined as the measured response
time for a full reorientation of the optic axis. (Note that for display devices\textsuperscript{17} $\tau$ is given as the time required for an optical transmittance change from 10\% to 90\% when the applied field polarity is reversed. However we have considered the full switching time, i.e., the time for optical transmittance change from 0 to 100 \%). A typical optical response curve is shown in Fig. 4.4. With this measured value of $\tau$ one can calculate $\gamma_\phi$ using the relation

$$\gamma_\phi = \tau P_s E$$  \hspace{1cm} (4.7)

\subsection*{4.3.2 Field reversal method}

The basis of these methods is that when the polarity of a driving electric field is reversed a transient current is induced due to the reorientation of the dipoles. This current contains the information about the dynamics of the polarization reversal and thus about the rotational viscosity. The expressions used to determine $\gamma_\phi$ depend on the shape of the applied field.

**Field reversal using square wave field**

The first attempt to measure $\gamma_\phi$ by this method was done by Skarp \textit{et al.},\textsuperscript{6} The response time $\tau$ was defined as the time between the square wave pulse edge and the peak position of the transient current. $\gamma_\phi$ was evaluated using the relation, $\tau = \gamma_\phi/(P_s E)$. Later Kimura \textit{et al.},\textsuperscript{18} utilising the equation given by Xue-Jie \textit{et al.},\textsuperscript{19}, introduced a correction factor and $\tau$ is given by $\tau = \tau_\omega/1.76$, where $\tau_\omega$ is the full width at half maxima (FWHM) of the current peak. Now several simplified analytic switching models\textsuperscript{19–22} exist enabling the evaluation of $\gamma_\phi$ from the polarisation reversal current. These models include considerations of the elastic (boundary) effects,\textsuperscript{20} dielectric torque,\textsuperscript{19} fluctuations\textsuperscript{21} and layer tilt.\textsuperscript{22} Of these models the model in which
Fig. 4.4. Optical response curve
elastic forces are considered predicts properly the position of the peak on the time axis and it also accounts for the sample alignment and thus one can determine $\gamma_\phi$ fairly accurately. Therefore we have adopted this model for the analysis of our field reversal current peak data.

In this model, the flexoelectric effect and the effect of variation in the dielectric constant during the polarization reversal are neglected. The elastic torque is defined in such a way that it is 0 for $\phi = \pi/2$, (where $\phi$ is the angle between the electrode normal and the direction of $P_e$ see Fig.4.5) which corresponds to the uniform orientation of $P_e$ and it is non-zero for $\phi = 0$ and $\kappa$. Such an elastic torque can be assumed to be proportional to $\cos \phi$ as for $\phi = \pi/2$, $\cos \phi = 0$ and for $\phi = 0$ and $\pi$, $\cos \phi$ is non-zero. $\gamma_\phi$, the viscosity which opposes the reorientation of the $P_e$ in an alternating electric field is assumed to be proportional to $\partial \phi / \partial t$. Thus one can write the torque equation for equilibrium as

$$- P E \sin \phi + K \cos \phi = \gamma_\phi \frac{\partial \phi}{\partial t}$$

where $K$ is an effective elastic constant.

By solving this equation one can get a relation for $\gamma_\phi$ as

$$\gamma_\phi = \frac{P E}{\kappa \cos \phi_0}$$

where

$$\kappa = \frac{1.76275}{\tau} \quad \text{and} \quad \tau = \tau_+ + \tau_-$$

$$\phi_0 = 2 \sin^{-1} \left[ \frac{\beta - (\beta^2 - 2\beta + 2)^{1/2}}{2(\beta - 1)} \right]$$

where $\beta = \exp (\kappa \tau_s)$.

The terms $\tau_s$, $\tau_+$ and $\tau_-$ are defined in Fig. 4.6. Using the same parameters one can
Fig. 4.5. Geometry of the cell defining parameters used to derive eqn. (3.9). (After Dahl et al., Ref. 20).
Fig. 4.6. Current response to an applied square wave field experimental curve for $D_8$. 
obtain an expression for the elastic constant $K$

$$K = P_z E \tan \phi_0$$

**Field reversal using triangular wave field**

To extract information about $\gamma_\phi$ from the transient current due to an applied triangular wave field we have adopted the model given by Escher *et al.* In this model the thermal fluctuations and interactions with the walls enclosing the liquid crystal are not considered.

Consider an uniformly aligned $C^*$ sample. Let $\mathbf{n}$ be the director and $\theta$ the tilt angle between $\mathbf{n}$ and layer normal $z$-axis. Let $xz$ be the substrate plane (see Fig. 4.7). When a field $\mathbf{E}$ is applied along $y$-direction the $P_z$ couples with the field and a torque $\mathbf{E} \mathbf{e}_y \times \mathbf{P}$, is set which rotates the molecule about the $z$-direction and this rotation is opposed by the viscosity.

The torque balance equation is

$$\dot{L} + \gamma_\phi \frac{\partial \alpha}{\partial t} + \mathbf{P}_{tot} \times \mathbf{E}_y = 0$$

where $L$ is the time derivative of the angular momentum $L$, which comes due to the moment of inertia of the molecules. As $L$ is small it can be neglected.

$$\gamma_\phi \frac{\partial \alpha}{\partial t} + \mathbf{P}_{tot} \times \mathbf{E}_y = 0$$

(4.11)

Here $\mathbf{e}_y$ is the unit vector along the $y$-axis. $P_{tot}$ is the total (spontaneous + induced) electric polarization. Since the magnitude of the applied field is not large, $P_{tot}$ is approximated by $P_z$. 

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Fig. 4.7. C' structure showing \( \vec{n}, \vec{P}, \) and \( \vec{C} \)
Hence

$$\gamma \phi \frac{\partial \alpha}{\partial t} + P_s \times \mathbf{E} = 0$$  \hspace{1cm} (4.12)$$

$$\gamma \phi \frac{\partial \alpha}{\partial t} + P_s E \sin \alpha = 0 \quad \text{or} \quad \frac{\partial \alpha}{\partial t} = -\frac{P_s E \sin \alpha}{\gamma \phi}$$  \hspace{1cm} (4.13)$$

As both \( E \) and \( \alpha \) are functions of time \( t \),

$$\frac{\partial \alpha}{\partial t} = -\frac{P_s E(t) \sin \alpha(t)}{\gamma \phi}$$

If \( J \) is the current density due to this spontaneous polarisation \( P_s \), one can write

$$J e_y = \frac{\partial P_s e_y}{\partial t}$$

as \( P_s = P_s \cos \alpha \) in the field direction

$$J = -P_s \sin \alpha(t) \frac{\partial \alpha}{\partial t}$$

Putting value of \( \frac{\partial \alpha}{\partial t} \) we get

$$J = -P_s \sin \alpha(t) \left(-\frac{P_s E(t) \sin \alpha(t)}{\gamma \phi}\right)$$

$$J = \frac{P_s^2 \sin^2 \alpha(t) E(t)}{\gamma \phi}$$

According to Escher et al.,\(^7\) for the determination of \( \gamma \phi \), it is sufficient to find \( J_{\text{max}} \), the maximum value of \( J \). It is given by

$$J_{\text{max}} = \frac{P_s^2 E_{\text{max}}}{\gamma \phi}$$
But \( J_{\text{max}} = I_{\text{max}} / A \), where \( A \) is the active area of the electrode.

Hence

\[
\frac{I_{\text{max}}}{A} = \frac{P_s^2 E_{\text{max}}}{\gamma_\phi} \tag{4.14}
\]

\[
\gamma_\phi = \frac{A P_s^2 E_{\text{max}}}{I_{\text{max}}} \tag{4.15}
\]

The output wave of the form shown in Fig. 4.8 gives the value of maximum current \( I_{\text{max}} \) and the corresponding electric field \( E_{\text{max}} \) is taken from the input field at that instant.

**Transient current response to an applied sine wave field (The hysteresis loop method)**

The method is based on the well known Sawyer-Tower method\(^{23} \) or the hysteresis loop method, which was modified by Diamant et al.\(^{24} \) The details of this method are already given in chapter II. Now we explain how \( \gamma_\phi \) can be determined by the hysteresis loop method.\(^8 \)

Consider the Diamant bridge circuit shown in Fig. 4.9. When a sine wave \( U_x = U_0 \sin \omega t \) is applied to the sample a hysteresis loop as shown in Fig. 4.10 is obtained. The amplitude of the output voltage \( U_y \) developed across the capacitor \( C \) (\( C = C_f \) of Fig. 4.9) gives the value of \( P_3 \). [Note that, when the bridge is balanced, the linear electric elements like ionic and capacitive induced currents are balanced by the compensating resistor \( R_C \) and capacitor \( C_C \).]

If \( A \) is the active electrode area then

\[
P_3 = \frac{C U_y}{A} \tag{4.16}
\]
Fig. 4.8. Current response to an applied triangular wave field - experimental curve for $D_8$. 
Fig. 4.9. (a) Experimental set-up on Diamant bridge technique. S: Signal source; X, Y: Sample leads; $R_c, C_c$: Compensating resistor, Capacitor combination; $C_f$: Fixed capacitor; OSC: Dual channel storage oscilloscope; ADC + DAS: Analog-Digital Converter and Data Acquisition System; PC: Personal Computer. AD524 is a programmable gain instrumentation operational amplifier.
Fig. 4.10. Current response to an applied sine wave field and the hysteresis loop - experimental curve for $D_8$. 
[Note that $U_y$ is the maximum of the output as the applied field goes through a cycle.] These parameters can be used in the following way to obtain $\gamma_\phi$ using the relation (4.15).

If $J_\text{m}$ is the maximum current density, then $I_\text{m} = A \cdot J_\text{m}$,

Also $J_\text{m} = \frac{\partial P_y}{\partial t} - \frac{\partial C U_y}{\partial t} - \frac{C \partial U_y}{A \partial t}$

But $\frac{\partial U_y}{\partial t} = \frac{\partial U_y}{\partial U_x} \times \frac{\partial U_x}{\partial t}$

Substituting for $U_x$,

$$\frac{\partial U_x}{\partial t} = -w U_o \cos wt$$

or

$$J_\text{m} = \frac{C \partial U_y}{A \partial U_x} \omega U_o \cos wt$$

or

$$I_\text{m} = AJ_\text{m} = C \omega U_o \cos \omega t \frac{\partial U_y}{\partial U_x}$$

(4.17)

Since $U_x = U_o \sin \omega t$

$$\frac{U_x^2}{U_o^2} = \sin^2 \omega t = 1 - \cos^2 \omega t$$

$$\cos \omega t = \frac{(U^2_o - U^2_x)^{1/2}}{U_o}$$

Therefore the maximum current $I_m$ is given by

$$I_m = C \omega U_o \left(\frac{U^2_o - U^2_x}{U_o} \right)^{1/2} \frac{\partial U_y}{\partial U_x}$$

(4.18)
Putting this in eqn. (4.15) we get

$$\gamma_\phi = \frac{A P_s^2 E_m}{C \omega (U_o^2 - U_x^2)^{1/2} \frac{d U_y}{d U_x}}$$

(4.19)

But \( P_s^2 = \frac{C^2 U_y^2}{A^2} \) and \( E_m = \frac{U_x^m}{d} \),

where \( d \) is the thickness of the cell.

Hence

$$\gamma_\phi = \frac{C^2 U_y^2 U_x^m}{A d} \frac{1}{C \omega (U_o^2 - U_x^2)^{1/2} \frac{d U_y}{d U_x}}$$

or

$$\gamma_\phi = \frac{C U_y^2 U_x^m}{A \omega d (U_o^2 - U_x^2)^{1/2} \frac{d U_y}{d U_x}}$$

(4.20)

Thus \( \gamma_\phi \) is expressed in terms of the known parameters of the hysteresis loop as shown in Fig. 4.10. Here \( U_x^m = U_x \) at \( U_y = 0 \) and \( U_y \) is the maximum value of \( U_y \).

From the hysteresis loop one can get the values of \( U_y, U_x \) at \( U_y = 0, \frac{d U_y}{d U_x} \) and the amplitude of the applied field, \( U_o \) and hence \( \gamma_\phi \) can be determined. An advantage of this method over the polarisation reversal methods is that the contribution coming from the linear electric elements is eliminated by the balance condition of the bridge.

A more appealing advantage is that in the same experiment one can simultaneously determine \( P_s, \gamma_\phi \) and the coercive field \( E_c \).

### 4.4 Materials

Measurements were done on six homologs (\( n = 7 \) to 12) of the series [2S,3S]-4'-((2-chloro-3-methylpentanoyloxy)phenyl trans-4''-n-alkoxy cinnamates.\(^{25}\) The structural formula and transition temperatures in (°C) for these compounds (short form \( D_n \))...
are already given in Table 2.1. The reason for choosing this series of compounds is that, as already observed in chapter II, the $P_s$ value of these compounds is high and the temperature range of smectic C* phase is also large for all the homologs. Further the critical field, necessary for unwinding the helix, is small ($\approx 10$ kV/cm) for all the homologs even at $T_c - T = 10^\circ C$.

4.5 Experimental

4.5.1 Preparation of the sample cell and alignment

The preparation of the sample cell and the method employed for obtaining good sample alignment have already been described in chapter II. During any measurement the temperature of the cell was kept constant to better than $\pm 5 mK$.

The different experimental set-ups used for the measurement of $\gamma_\phi$ are described below.

4.5.2 Optical transmission method

The experimental set up used for this experiment is shown in figure 4.11. A homogeneously well aligned sample cell is placed between a polariser and an analyser. A He-Ne laser (Spectra Physics 120S) with a low amplitude drift was used as the source. The transmitted intensity was detected with a fast response (rise time $\sim 10$ ns) and low dark current photodiode (Centronics OSI5). A square wave pulse applied to the sample switches the director by an angle $2\theta$ ($\theta$ being the tilt angle) when its polarity is reversed. The output of the photodiode and the applied square wave signal were fed to a storage oscilloscope (Philips PM2203) which was triggered by the positive leading edge of the applied signal. The data acquired was then transferred to a microcomputer for storage and analysis. By setting the polariser and
Fig. 4.11. Set-up for optical response time measurements.
analyser properly perfect light modulation can be obtained from which the exact switching time can be determined. A typical response curve is shown in the figure 4.4. Since our interest is to compare optical and nonoptical methods of obtaining $\gamma_\phi$ values, we took the 0-100% intensity variation time as the switching time $\tau$ rather than the usually used 10-90% time.

### 4.5.3 Transient current response to an applied square wave field

The experimental set up used is shown in figure 4.12. The function generator used (HP 8116) could deliver a maximum amplitude 32 V peak to peak (which was sufficient to generate fields as high as $\approx 30$ kV/cm). The square wave field when applied to the sample causes a reversal of the dipoles when its polarity is reversed. The current associated with this reversal is measured as a voltage drop across the current sensor resistor $R_s$ connected in series with the sample. The value of $R_s$ should be carefully selected such that it makes a negligible contribution to the RC time constant of the cell. The output and input signals were fed to a dual channel storage oscilloscope PM 2203. The data acquisition and control was handled by a microcomputer. Fig. 4.6 is a typical field reversal current peak in which different parameters involved in the calculations of $\gamma_\phi$ are defined.

### 4.5.4 Transient current response to an applied triangular wave field

Basically the experimental set up and the data acquisition process are similar to the square wave method. The input wave and the sample response are shown in fig. 4.8. By finding the maximum current $I_{\max}$ and the corresponding applied field $E_m$, the value of $\gamma_\phi$ was evaluated.
$S$ - Signal source  
FLC - Ferroelectric Liquid Crystal Sample cell  
$R_s$ - Current sensor resistor  
OSC - Dual channel memory oscilloscope  
PC - Personal Computer

Fig. 4.12. Block diagram for the field reversal techniques.
### 4.5.5 Hysteresis loop method

For this method a calibrated Diamant bridge (described earlier in chapter II) was used to obtain the D-E hysteresis loop of the sample due to an applied sine wave field. By adjusting the value of the resistor $R_C$ and capacitor $C_C$ one can compensate for the ionic and capacitive contributions and obtain a hysteresis loop as shown in the Fig. 4.10. The data acquisition and analysis were handled by a high resolution data acquisition system (HP7090A) and a computer as explained in chapter II. With the help of the hysteresis loop it is possible to obtain the different parameters needed to calculate $\gamma_\phi$ as defined in the Fig. 4.10.

### 4.6 Results and Discussion

#### 4.6.1 Comparison of $\gamma_\phi$ values obtained by different techniques

Figure 4.13 is an arrhenius plot of $ln \gamma_\phi$ vs. $1/T$ for the 8th homolog of the $D_n$ series. Here we have plotted the $\gamma_\phi$ values obtained by the four different methods described above. It is clearly seen that throughout the range of the measurement there is excellent agreement between the $\gamma_\phi$ values determined from the different techniques. Further it is seen that except close to the $A\cdot C^*$ transition temperature $T_{AC^*}$ the behaviour is of Arrhenius type. Thus the temperature variation of $\gamma_\phi$ can be expressed as $\gamma_\phi = \gamma_{\phi_0}e^{\mu/kT}$, where $\mu$ is the activation energy. The value of $\mu$ obtained by fitting the data away from $T_{AC^*}$ to the above equation is $\mu = 1.62$ eV. Close to the transition the behaviour is non-Arrhenius and a power law type of expression may describe the data better than the Arrhenius law. However, a single exponent does not seem to describe the data over a wide range of temperature. This may probably be due to the mean field to tricritical cross-over behaviour generally
**Fig. 4.13.** Comparative plot of $\ln \gamma_\phi$ versus $1/T$ for $D_8$ obtained by four techniques discussed in the text.
observed near the A-C* transition.

### 4.6.2 Effect of Chain Length

In Fig. 4.14 we have plotted $\ln \gamma_\phi$ as a function of $1/T$ for the six homologs of the series ($n = 7$ to 12). In this plot we present only the results obtained using the hysteresis loop method which, as we showed in the previous section, agree very well with the values determined by the other methods. The reasons for choosing the hysteresis loop method are following: (1) The advantage of using the hysteresis loop method as compared to the polarization reversal method is that the background current coming from the linear electric elements need not be taken into account or subtracted numerically which pose inconvenience in the exact determination of $\gamma_\phi$. In the hysteresis loop method these linear electric elements are eliminated by the balance condition of the bridge. (2) In the same run one can collect the information about $P_s$ and $\gamma_\phi$. In Fig.4.14 we have normalised the plots by assuming a single $T_c$ to facilitate comparison between different homologs. The notable features are (1) there is a systematic variation of $\gamma_\phi$ with chain length. (2) Similar to the 8th homolog, the overall variation of the $\gamma_\phi$ appears to be of power law type. But if the data away from the $T_c$ is considered it appears to follow Arrhenius law. It is clear from the Fig.4.14 that away from the transition the slope of the plots and hence the activation energy is approximately the same for all the homologs, showing thereby that although the absolute value of $\gamma_\phi$ is very much influenced by the chain length, its temperature variation is the same for all the homologs. This perhaps suggests that the alkyl chain length is responsible only for the absolute value of $\gamma_\phi$ whereas its temperature variation is independent of $n$ and controlled by the rigid core. Fig.4.15 shows $\gamma_\phi$ (at $T_c - 5^\circ C$) as a function of chain length for all the homologs $n=7$ to 12. From the figure it is seen that $\gamma_\phi$ decreases rapidly with $n$ for lower homologs and...
Fig. 4.14. Plot of $ln\gamma$ versus $1/T$ for the six homologs $D_7$ to $D_{12}$. 
but appears to reach a lower limit and stabilize for longer chain lengths. However, the $P_s$ variation with $n$ is different in that it varies linearly with $n$ as seen from the Fig.4.16. Using the relation $\tau = \gamma_\phi/P_sE$ we have calculated for all the homologs the value of $\tau$ at $T_c - 5^\circ C$ at an applied field value of 50 kV/cm. The plot of $\tau$ vs. $n$ is shown in Fig. 4.17. It is clear from the figure that $\tau$ is very much sensitive to the chain length for lower homologs and it reaches a limiting value for the higher homologs. The limiting value may perhaps be imposed by the rigid core. This suggests that while selecting materials for fast response the limitation imposed by the rigid core should also be kept in mind.

In order to study the effect of subtle changes in the molecular structure on the value of rotational viscosity $\gamma_\phi$ and the rise time $\tau$ we have measured the $\gamma_\phi$ and $\tau$ for 10th homologs of the four series which have almost similar molecular structure (series A, B, C and D) discussed in Chapter II. In Figs. 4.18a-4.18d, we have plotted $\tau$ vs $(T_c - T)$ for the 10th homolog of the four series obtained with a field of 30 kV/cm. The figures show that in all the four series $\tau$ varies in a non-linear fashion as the temperature is changed. The variation of $\tau$ is steeper in series A and B compared to series C and D. Comparing the values obtained at $T_c - T = 5^\circ C$ we see that series D has the smallest value $\simeq 25\mu$sec and series C has 45 $\mu$sec whereas series A and B have the same value $\simeq 60\mu$sec. Thus one can probably conclude that in order to reduce the switching time it is better to cluster the chiral groups together and attach them directly to the core. This also happens to be the criterion for getting higher polarization values as we have seen in Chapter II.

Figures 4.19a-4.19d show the plots of $\gamma_\phi$ and $\gamma_G = \gamma_\phi/\sin^2 \theta$ as a function of temperature for the 10th homolog of tlc each series calculated at a field of 30 kV/cm. It is seen that the values of $\gamma_\phi$ and $\gamma_G$ are not very different for the four
Fig. 4.15. Dependence of $\gamma_0$ on chain length at $T_c - 5^\circ C$.

Fig. 4.16. Dependence of $P_s$ on chain length at $T_c - 5^\circ C$. 
Fig. 4.17. Dependence of response time $\tau$ on chain length at $T_c - 5^\circ C$. 
Fig. 4.18. Response time as a function of temperature for \( n = 10 \) of (a) series \( D_n \), (b) series \( B_n \), (c) series \( C_n \) and (d) series \( A_n \).
Fig. 4.19. Rotational viscositirs $\gamma_\beta$ and $\gamma_\psi$ versus temperature for $n = 10$ of (a) series $A_n$, (b) series $B_n$, (c) series $C_n$, and (d) series $A_n$. 
compounds, e.g., at $T_c - 5^\circ C$, $\gamma_\phi \approx 40mPaS$. However the variation of $\gamma_G$ with temperature is different for series A and B. For series A and B the $\gamma_G$ variation is very small with temperature. This confirms the statement made earlier that $\gamma_G$ is the true rotational viscosity and one has to take $\gamma_\phi$ and not $\gamma_\phi$ while considering the temperature variation of the rotational viscosity. (In fact, as we shall see later in Fig.4.24, the data collected at close intervals of temperatures brings out this feature beautifully.) However for series C and D $\gamma_G$ varies initially and appears to attain a steady value at lower temperatures.

In order to do a quantitative comparison of the effect of $P_s$ on $\gamma_\phi$, we have calculated a quantity $P_s/\gamma_\phi$ which is the inverse of the product $P_s/\gamma_\phi$; the greater the value of $P_s/\gamma_\phi$ the better will be the switching. In table 4.1 we have tabulated $P_s/\gamma_\phi$ for $n = 10$ of each series. The table shows that series D, having 2 chiral groups near the core, has the highest value of $P_s/\gamma_\phi$. The value $P_s/\gamma_\phi = 0.025 \text{ C/m}^2\text{PaS}$ for $n = 10$ of series D compares fairly well with the values reported by Otterholm et al., and Chandani et al., (0.04 and 0.06 C/m$^2$PaS respectively).

### 4.6.3 Soft Mode Viscosity $\gamma_s$

Unlike $\gamma_\phi$, there are only a few studies$^5,9$ of $\gamma_s$, the viscosity associated with tilt amplitude fluctuations. In most of the earlier studies $\gamma_s$ was determined by the pyroelectric method. We have adopted the dielectric dispersion method for the determination of $\gamma_s$. As we have seen in chapter III the generalized mean field model predicts$^29$ the following relation for the strength and relaxation frequency of the soft mode (neglecting $\epsilon \mu^2$ term)

$$\epsilon_s \Delta \epsilon_s = \frac{(\epsilon_0 C \epsilon)^2}{\alpha (T - T_c) + K_3 q_0^2}$$ (4.21)
Table 4.1

$P_s/\gamma_\phi$ ratios for the 10th homologue
(at $T_c - T = 5^\circ C$) of each series

<table>
<thead>
<tr>
<th>Compound</th>
<th>$P_s/\gamma_\phi$ (C/m² Pa.s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₁₀</td>
<td>0.009</td>
</tr>
<tr>
<td>B₁₀</td>
<td>0.008</td>
</tr>
<tr>
<td>C₁₀</td>
<td>0.015</td>
</tr>
<tr>
<td>D₁₀</td>
<td>0.025</td>
</tr>
<tr>
<td>Lactic acid derivatives²</td>
<td>0.06</td>
</tr>
<tr>
<td>MIPOBC²⁸</td>
<td>0.04</td>
</tr>
</tbody>
</table>
\[ f_s = \frac{\alpha(T - T_c) + K_3 q_o^2}{2\pi\gamma_s} \]  

(4.22)

where \( \Delta \epsilon_s \) and \( f_s \) are the strength and relaxation frequency of the soft mode. \( C \) is the bilinear coupling term, \( K_3 \) an elastic constant, \( q_o \) the helical wave vector at the transition and a the coefficient of the temperature dependent term in the Landau expansion, \( \epsilon_o \) the permittivity of the free space and \( \epsilon \) the high temperature dielectric constant.

Multiplying (4.21) and (4.22)

\[ \epsilon_o \Delta \epsilon_s f_s = \frac{\epsilon_o^2 C^2 \epsilon^2}{2\pi\gamma_s} \]  

(4.23)

or

\[ \gamma_s = \frac{\epsilon_o^2 C^2 \epsilon^2}{2\pi\Delta \epsilon_s f_s} \]  

(4.24)

We have measured the \( \Delta \epsilon_s, f_s \) and \( \epsilon \) by the dielectric method as described in chapter III. Since the coupling coefficient \( C \) is not known we define a quantity \( \eta \) as

\[ \gamma_s \propto \eta = \frac{\epsilon^2}{2\pi\Delta \epsilon_s f_s} \]  

(4.25)

The \( \eta \) values computed using eqn. 4.25 are plotted in Fig. 4.20 for the 7th and 12th homologs of the series. Here we have presented the \( \gamma_s \) results in smectic A phase only. From the figure it is obvious that the value of \( \eta \) is more for \( D_{12} \) than \( D_7 \). But overall temperature variation of \( \eta \) is the same for both the compounds indicating that there is no significant change in the rate of variation of \( \eta \) with temperature as the chainlength \( n \) is increased.

Figures 4.21 and 4.22 are the arrhenius plots of \( \ln \eta \) vs. \( \ln(1/T) \) for \( D_7 \) and \( D_{12} \). Similar to \( \gamma_s, \eta \) also behaves in a non-arrhenius fashion close to the transition.
Fig. 4.20. Temperature dependence of $\eta$ for $D_7$ and $D_{12}$. 
Fig. 4.21. Arrhenius plot of $\eta$ for $D_7$. 
Fig. 4.22. Arrhenius plot of $\eta$ for $D_{12}$. 
For the data away from $T_c$ we have fitted a straight line, the slope of which gives a measure of the activation energy. Within experimental errors, the slopes and thus the activation energies for the two compounds are the same, indicating that the tilt fluctuations are hardly influenced by the increase in chain length. Since the coupling coefficient is not known, it was not possible to find the absolute value of $y$. However we have determined the absolute value of $\gamma_s$ for another compound $C_6$ (the 6th homologue of the $C$ series; see Table 2.3). For this compound we have obtained $y_s$ by the dielectric method. The value of $C$ was obtained by the procedure explained already in chapter III which enabled the determination of $y_s$. We have plotted $\ln \gamma_s$ vs. $T - T_c$ in Fig. 4.23. It is seen that $\gamma_s$ diverges at the transition. We have fitted the data of $\gamma_s$ to an expression of the form

$$\gamma_s = A(T - T_c)^x + \gamma_0 \exp(B/T)$$

(4.26)

where the last term in RHS is the usual Arrhenius background contribution. The fit gives a value of $x = -0.27$. The value of $x$ obtained for this compound is same as that obtained by Gouda et al.\textsuperscript{30} for another compound.

We have also determined $\gamma_\phi$ and $\gamma_G$ for this compound by employing the hysteresis loop method. A semilog plot of $\gamma_\phi$, $\gamma_G$ versus $T_c - T$ is shown in Fig. 4.24. The temperature dependence of these two quantities confirms our earlier conclusion that it is $\gamma_G$ which is of more fundamental importance. Furthermore it is seen, from Fig. 4.23 and 4.21, that the value of $\gamma_s$ is an order of magnitude greater than the value of $\gamma_\phi$, which is in a good agreement with the results of Pozhidayev \textit{et al.}\textsuperscript{5}
Fig. 4.23. Temperature dependence of soft mode viscosity $\eta_s$; squares represent the experimental data and the line shows the fit to eqn. (4.26).
Fig. 4.24. Variation of $\gamma_\phi$ (+) and $\gamma_G$ (□) as a function of temperature. Note that $\gamma_G$ shows Arrhenius behaviour right up to the transition.


References


