SOME ELECTRIC AND MAGNETIC FIELD EFFECTS IN LIQUID CRYSTALS

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Doctor of Philosophy
in the Faculty of *Science*

by

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DECLARATION

I hereby declare that the entire work embodied in this thesis is the result of the investigations carried out by me independently in the Liquid Crystal Laboratory, Raman Research Institute, Bangalore, and that no part of it has been submitted for the award of any Degree, Diploma, Associateship or any other similar title.

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CERTIFICATE

I certify that this thesis has been composed by Mr. P. R. Maheswara Murthy based on the investigations carried out by him at the Liquid Crystal Laboratory, Raman Research Institute, Bangalore, under my supervision. The subject matter of this thesis has not previously formed the basis of the award of any Degree, Diploma, Associateship, Fellowship or other similar title.

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TO

MY BELOVED PARENTS

MAHESH

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PREFACE

We describe in this thesis some investigations on the effect of electric fields on nematic liquid crystals (NLC). Xlagnetic fields have been employed only to align the liquid crystals in specific directions in some experiments. Two chapters of the thesis are on electrohydrodynamic instabilities [EHD] in NLC in which flexoelectricity plays an important role. In the last two chapters we have described electrooptic techniques of measuring anchoring energies corresponding to tilt and azimuthal orientations, making use of the electric field induced director deformation due to the flexoelectric effect. In the fourth chapter we report measurements of flexoelectric coefficients of a number of nematogenic compounds.

In Chapter I, a general introduction to liquid crystals is given with an emphasis on NLC. The relevant physical properties of nematics are described. Since a major part of this work is related to EHD instabilities and flexoelectric effect, a general theoretical and experimental background to these phenomena is also given.

In Chapter II we describe a propagating electrohydrodynamic instability that occurs in a nematic liquid crystal at the threshold of DC excitation if the symmetry of a planar aligned cell is changed by introducing a small pre-tilt of the director.

Electroconvective instabilities are observed in nematic liquid crystals with negative or weakly positive dielectric anisotropy ($\Delta\epsilon$) and positive conductivity anisotropy ($\Delta\sigma$) when subjected to an electric field (Blinov, 1983). In the widely studied geometry, a thin homogeneously aligned nematic sample is subjected to an electric field applied across its thickness. A small bend fluctuation of the director field (Helfrich, 1969) leads to space charge formation due to conductivity anisotropy and gives rise to electroconvective instability, commonly known as Williams domains (Chandrasekhar 1977) and when the field is above a critical value.

It is well known that the rubbing technique employed to produce homogeneous alignment results in a small pre-tilt (– 0.01 radian) of the director at the bounding surfaces (Mosley *et* ***al.***, 1987). We have theoretically shown that the EHD instability obtained in such a sample under DC excitation is not stationary but *propagates* in a direction normal to the roll axis. The propagation direction depends on the sign of the applied field, the tilt angle and that of the combination $(e_1 + e_3)$ of the flexoelectric coefficients. We use linearised EHD equations, consisting of (a) the Poisson equation, (b) the charge continuity equation, (c) the torque balance equation, and (d) the equation of motion. Both one- and two-dimensional calculations have been made to get the conditions for onset of the instability. The physical mechanism responsible for the propagating instability is due to an additional flexoelectric torque which is $\pi/2$ radians out of phase with the main torques responsible for EHD instability (Fig.1).

Experiments were conducted using cells made of ITO coated glass plates treated with polyimide and rubbed unidirectionally. We obtained propagating EHD rolls at an appropriate applied voltage. The propagation direction reversed when the field was reversed (Fig.2). The velocity of propagation was comparable with that calculated from theory.

The main result of Chapter III is a theoretical analysis of the EHD instabilities of a homogeneously aligned NLC subjected to a *transverse* AC electric field. We also present the results of our experimental investigation in this geometry.

Under an AC electric field the instabilities observed in the standard geometry are classified into two regimes, namely, *conduction regime* observed at lower frequencies and *dielectric regime* observed above a cut off frequency. The space charges oscillate with the field and the distorted director field remains practically stationary in the conduction regime. On the other hand, it is the director distortion that oscillates with the applied field, while space charges remain practically at rest in the dielectric regime. The Orsay

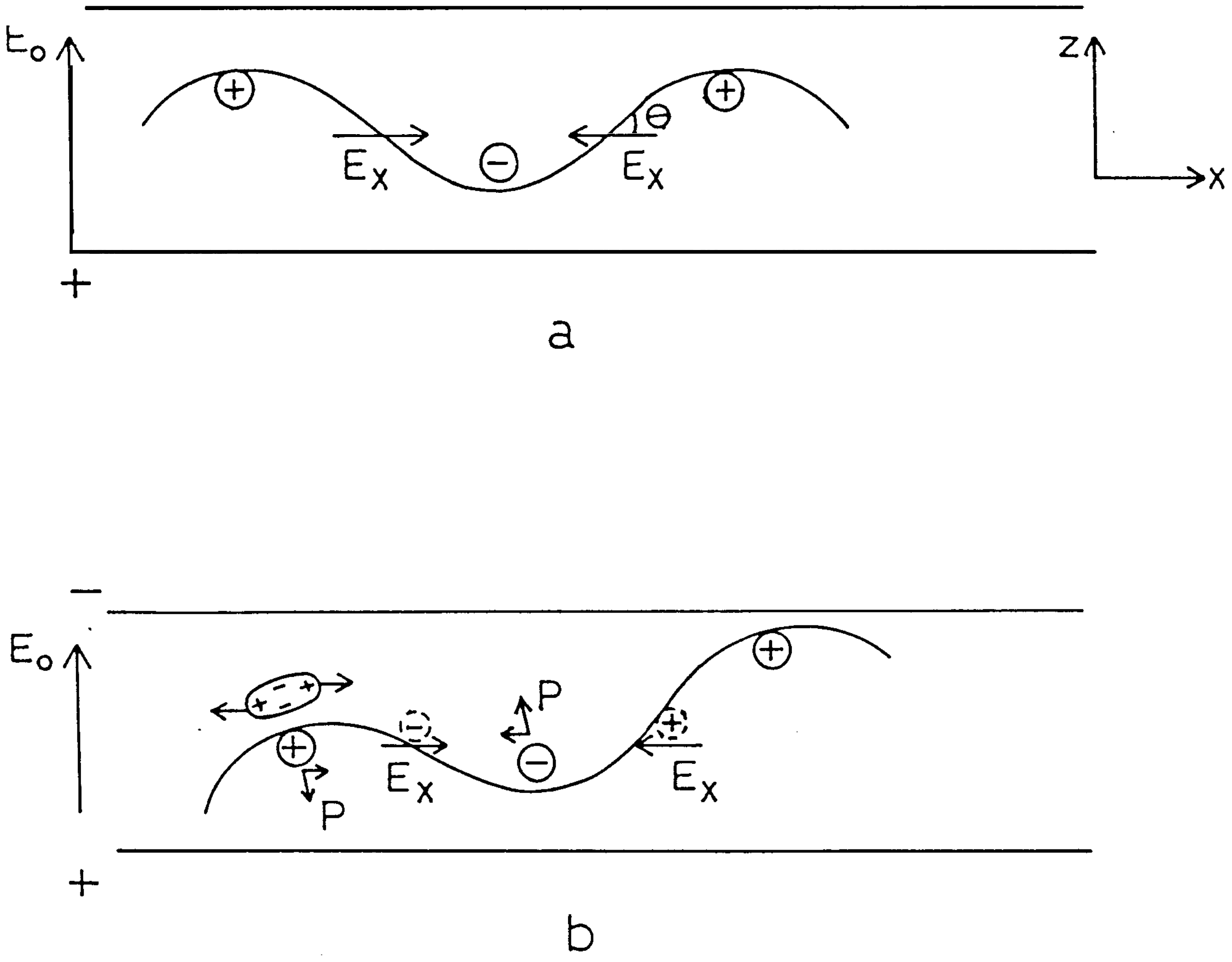

Fig.1: (a) β=0, the space charges (shown in full circles) arising from the conductivity anisotropy cause EHD instability. (b) When $\beta \neq 0$, the quadrupoles develop an out of phase torque due to the horizontal field gradients and additional charges (in dotted circles) are collected due to divergence of the flexoelectric polarisation $\vec{P}$.

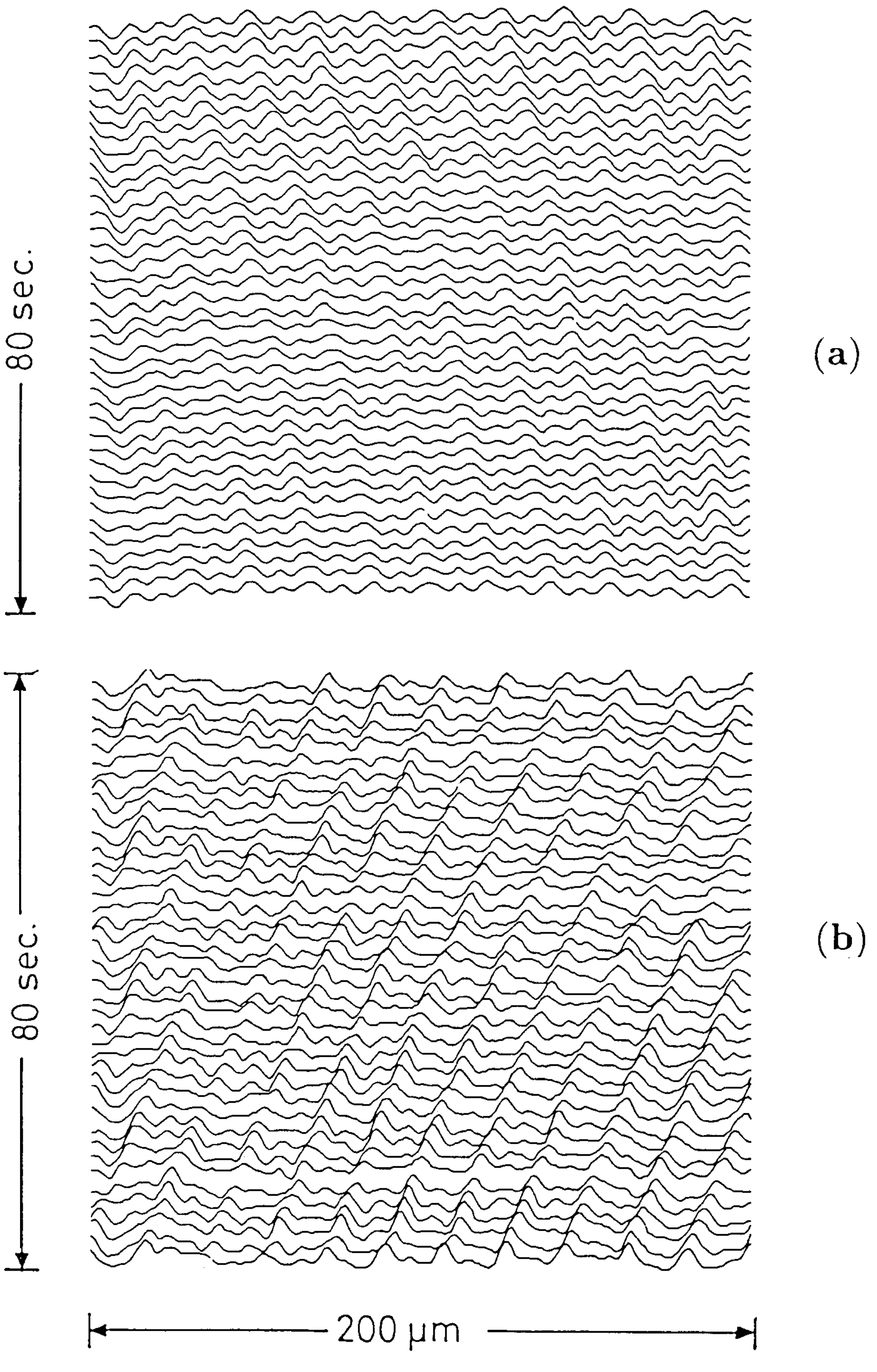

Fig.2: The light intensity profiles along a line normal to the rolls recorded at intervals of 2 secs. plotted on top of one another. (a) V=-8.9 volts, (b) V=+8.9 volt (V_{th}=8.5 volt). Note that the rolls propagate in opposite directions for opposite signs of the voltage. Thickness of the cell = 15 μm, temperature = 333 K.

model (Dubois-Violette et al., 1971) gives a satisfactory explanation of these instabilities in the standard geometry. Further calculations (Madhusudana et al., 1987, 1988; Kramer et al., 1989) including flexoelectric effect (Raghunathan and Madhusudana, 1988) have shown that in the conduction regime the director field develops additional twist distortion resulting in the formation of oblique rolls. In chapter III we describe electroconvective instabilities in a different geometry, i.e., with the field applied in the plane of the nematic and normal to the undistorted director. In this case the space charges are created by a periodic twist-bend distortion of the director field. Figure **3** shows the threshold *vs.* frequency diagram which has been calculated using the appropriate boundary conditions. Though there are many similarities between this diagram and the one for the standard geometry, there are also some important differences as discussed in chapter III. We have also done some experiments in this geometry. There is a broad agreement between the theoretical and experimental results.

A macroscopic polarisation can be induced in a nematic liquid crystal by splay and bend distortions of the director field. As was first shown by Meyer (1969), this flexoelectric polarisation is given by

$$\mathrm{P} = e_1\vec{n}(\nabla.\vec{n}) + e_3(\nabla \times \vec{n}) \times \vec{n}$$

where e_1 and e_3 are the two flexoelectric coefficients corresponding to splay and bend distortions respectively. In some geometries, the director profile of a nematic liquid crystal in an electric field is strongly influenced by flexoelectricity and this can be made use of in the measurement of e_1 and e_3.

In Chapter IV we describe the measurement of the flexoelectric coefficients of some nematic liquid crystals belonging to different homologous series. For the measurement of the combination $(e_1 - e_3)$, we have used the method of Dozov et al. (1982). In the experiment we use a hybrid aligned cell in which one of the plates is coated for homogeneous alignment and other for homeotropic alignment. The director of the nematic

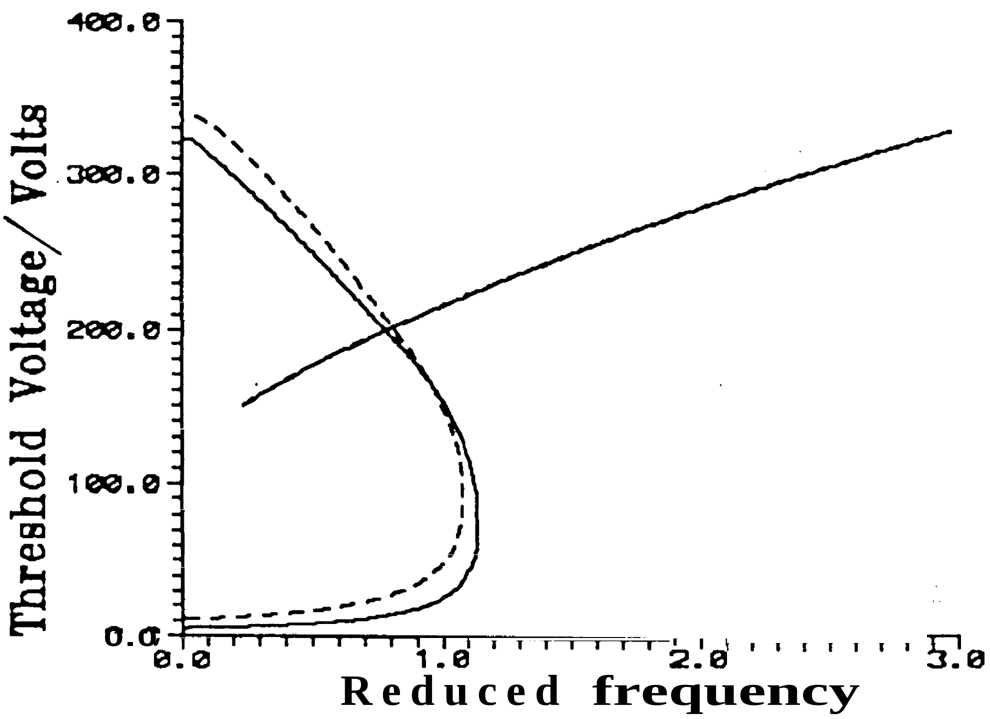

Fig.3 Variation of the threshold voltage with reduced frequency obtained from the calculations using MBBX parameters. d=50 μm. Lateral separation between the electrodes is 60 μm. The cut off frequency $f_c = 2\sigma_{||}/\epsilon_{||}$.

lies in the XZ plane. The anchoring at the two surfaces is assumed to be strong. The director field in such a cell has a permanent splay-bend distortion, which gives rise to a flexoelectric polarisation P along X, and given by $\mathbf{P} = (e_1 - e_3)\mathbf{n}(\nabla.\mathbf{n})$. When an electric field E is applied along Y, a twist distortion is created in the medium due to the action of E on P. Now if a light beam, which is linearly polarised along X, is allowed to be incident on the glass plate which is treated for homogeneous alignment, the polarisation direction of the transmitted beam will be rotated by an angle $\phi(0)$ due to the waveguide property of the twisted director field (hlauguin, 1911). $(e_1 - e_3)/K$ is obtained from the slope of the plot of twist angle vs. E. The sign of $(e_1 - e_3)$ can be deduced from the sign of twist for a given sign of E. Using this technique we have measured e^*/K, where $e^* = (e_1 - e_3)$, for a number of compounds. The main results are as follows:

a) e^*/K has a positive sign in practically all the compounds, except cyano cyclohexyl cyclohexane (CCH-7), which has a negative value. We have argued that in compounds like phenyl cyclohexane (PCH) and cyanobiphenyl (CB) series. the overall structure of a molecule is bowed and the end cyano group will give rise to a transverse component of dipole moment (see figures 4.21 and 4.22 in Chapter IV). This in turn gives rise to a positive sign for e^*/K. But in the case of CCH-7, the highly polar cyano end group makes a large angle with the long axis of the molecule and gives rise to the negative sign of e^*/K.

b) In most of the compounds, e^*/K is independent of temperature as is expected from theoretical models. This implies $e^* \propto S^2$, S being the orientational order parameter.

c) However compounds like CCH-7 and EPPC (ethoxyphenyl propyl cyclohexyl carboxylate), whose molecules have flexible cores show a temperature dependence of e^*/K. In CCH-7 we find that $e^* \propto S$. This trend probably arises from an increase in the flexibility of the molecules with temperature (see figures 4.23a and b in Chapter IV).

d) The magnitude of e^*/K decreases when we go from a two benzene ring system (say

5CB) to a three benzene ring system (say 5CT - pentylcyano terphenyl). The three benzene ring systems have a high nematic-isotropic transition temperature at which the alkyl chain can no longer be considered to be in an all-trans configuration. Thus the shape of the molecule is no longer bowed and hence e^*/K decreases in magnitude.

We have used another method of Dozov et al. (1984) for the measurement of the sum $(e_1 + e_3)$ of flexoelectric coefficients. A field gradient is produced by a quadrupolar arrangement of electrodes. The nematic is aligned homeotropically with strong anchoring at both the plates and the field gradient gives rise to a bend distortion described by the angle 8, which is estimated by measuring the tilt of the conoscopic pattern (θ) observed between crossed polarisers of a polarising microscope. $(e_1 + e_3)/K$ can be calculated from θ. There have been a few earlier measurements of $(e_1 + e_3)$. In most of them the sign of $(e_1 + e_3)$ has not been measured. We have determined the sign of $(e_1 + e_3)$ for several compounds.

In chapter V we describe an AC electric field technique for the measurement of relative anchoring strengths for tilt orientation at the two surfaces of a hybrid aligned (HAN) cell filled with a nematic liquid crystal.

The anchoring energy is a measure of the strength of the surface forces to impose a well-defined direction on the director $\hat{n}$ of the liquid crystal at the surface (de Gennes, 1974). It depends on the chemical nature of the liquid crystal and on the treatment given to the surfaces of the cell. In the case of strong anchoring the potential energy profile has a sharp minimum as a function of the angle 8. On the other hand, in the case of weak anchoring, the potential energy has a broad minimum.

We have studied CCH-7, PCH-7 and 7CB making use of HAN cells. In a HAN cell the director field of NLC given by $\theta(z)$ has a splay-bend distortion. We first measured the path difference (P.D.) of the cell, as a function of temperature, using a tilting compensator (Fig.4). In CCH-7 and PCH-7 the measured value of P.D. is found to be higher than its theoretical value calculated by assuming an ideal HAN cell with angles 0 and $\pi/2$ radians at the surfaces treated for homeotropic and homogeneous alignments respectively. This implies that the anchoring at the surface treated for homeotropic alignment is weaker than that at the other surface. Assuming that the anchoring energy for homogeneous alignment is strong it is clear that at the other surface the director deviates from the ideal homeotropic alignment. We have analysed the experimental data to calculate the anchoring energy at the homeotropic surface as a function of temperature (Fig.5).

We have also developed an AC electrooptic technique to estimate the anchoring energy at both the surfaces of the cell. The flexoelectric contribution to energy density depends linearly on curvature of the nematic director and it does not contribute to the bulk torque if there is only tilt distortion in the sample. In such a case flexoelectricity gives rise to a surface torque which produces a measurable effect only if the anchoring is weak and this is exploited to measure the anchoring energies.

Applying an AC field between ITO coated glass plates of the HAN cell, we have monitored the optical signals at the frequency (f-signal) and also at twice the frequency (2f-signal) of the applied field, using a photodiode and a lock-in-amplifier. In these measurements, the plane containing the director makes an angle of 45° with the crossed polarisers.

The following observations have been made with cells in which the homogeneous alignment was obtained by unidirectional rubbing of a polyimide coated glass plate and the homeotropic alignment by treating the plate with ODSE (octadecyl triethoxy silane).

1. As is shown in figure 6 for CCH-7, the f-signal increases up to a maximum value with the applied field and then falls to a minimum, before rising again with the field.
2. The 2f-signal steadily increases with the field initially, and after attaining a broad maximum falls off gradually.

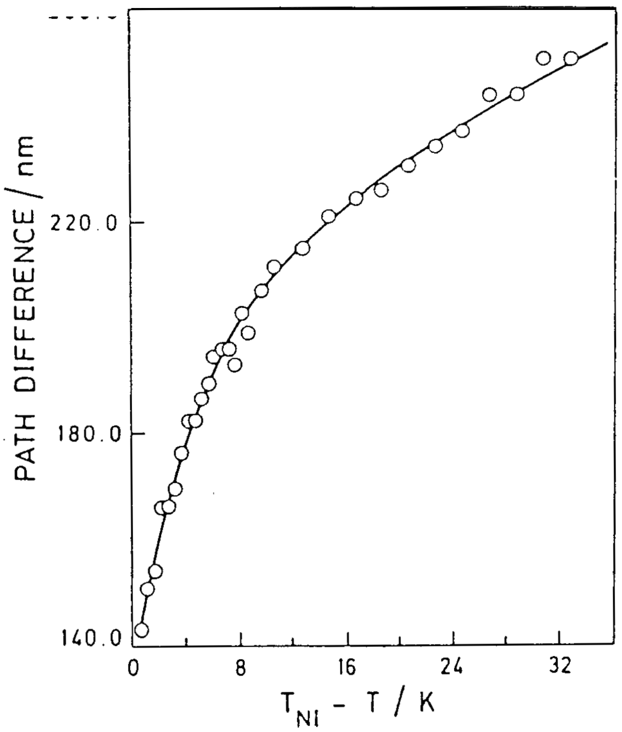

Fig.4: Variation of optical path difference (Al) with temperature of CCH-7. Cell thickness = 6.3 μm.

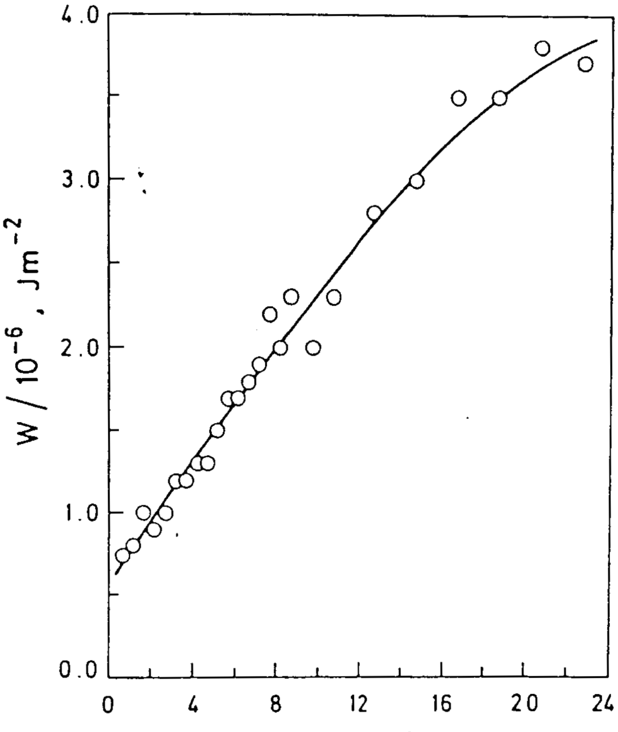

Fig.5: Temperature variation of anchoring energy at the homeotropically aligned surface of CCH-7. Sample thickness = 6.3 μm.

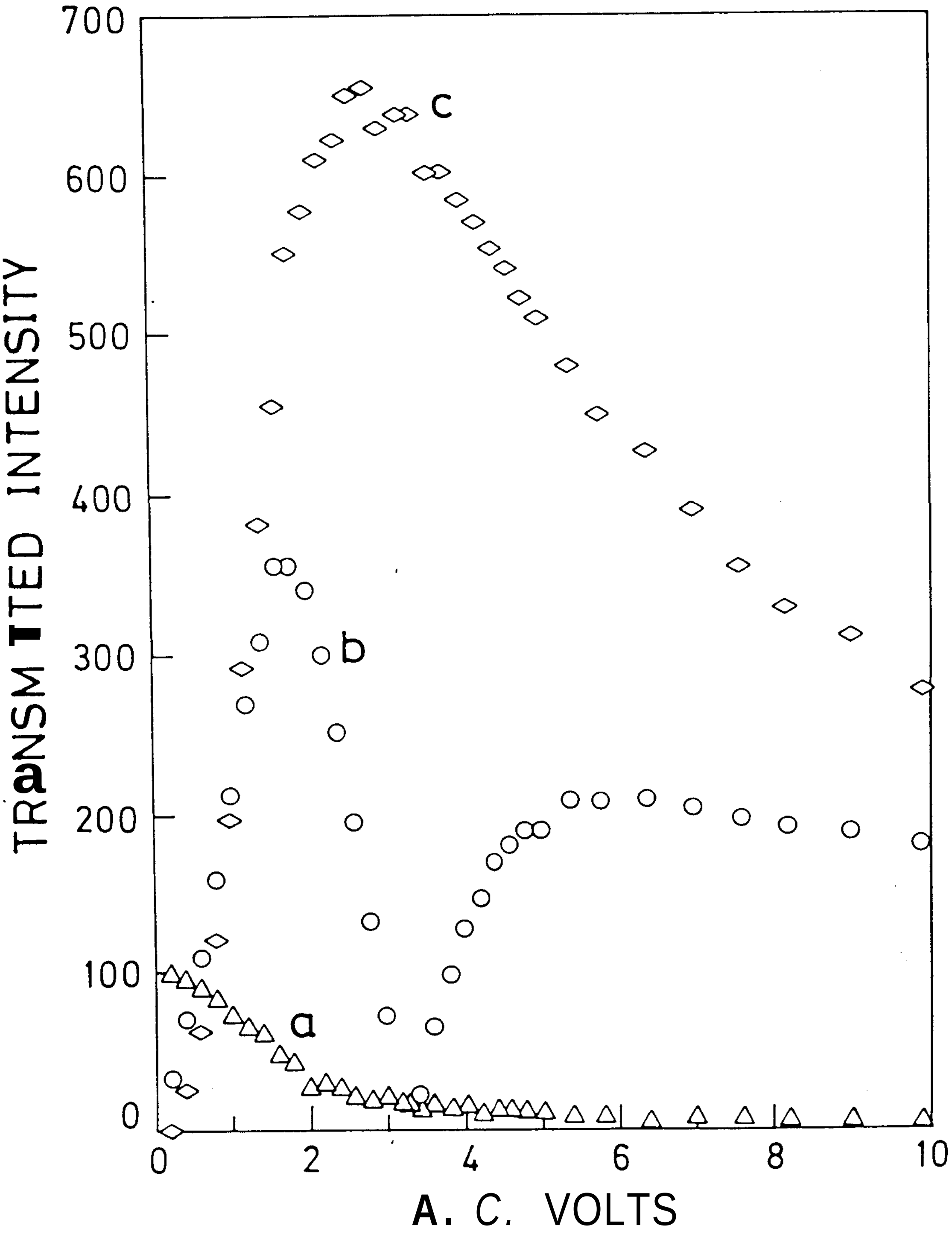

Fig.6: RMS voltage dependence of the DC (a: vertical scale in $\times 10^{-1} mV$), f (b: vertical scale in μV) and 2f (c: vertical scale in μV) components of the optical signal in CCH-7 at **333** K. Sample thickness = 6.3 μm, frequency = 23 Hz.

3. The DC component of the optical signal decreases as the field increases.

The flexoelectric contribution to the surface torque is proportional to $E \sin 2\theta_s$, where E is the electric field and 8, is the angle made by the director at the surface with the surface normal. This in turn gives rise to the f signal. The f signal produced at lower fields is due to 8 oscillations of the director which is weakly anchored at the homeotropic plate, and the signal increases linearly with the field. At higher fields, due to the dielectric torque, 8 decreases and approaches zero at the homeotropic plate resulting in a decrease in the f signal. The strong dielectric torque however decreases the angle 8, made by the director at the homogeneous plate to values lower than $\pi/2$. The flexoelectric torque at this surface now produces an f signal which starts rising (Fig.6). We have developed a simplified model to qualitatively account for these experimental trends and also to estimate the anchoring energies for tilt orientations at the two surfaces. Similar measurements have been made on PCH-7 and 7CB and the results are compared with the calculations.

We have found that in CCH-7 and PCH-7 the ODSE coating results in relatively weak anchoring when compared to the homogenous anchoring produced by polyimide coating. PCH-7 has a somewhat stronger homeotropic anchoring compared to CCH-7. In 7CB we have found that the anchoring energies at the two plates are relatively strong and comparable to each other.

In chapter: VI we describe a method for the measurement of anchoring energy for azimuthal orientation of the nematic director. We apply a transverse AC electric field on a nematic sample which has a non-uniform director alignment due to different pretilt angles at the two walls of the cell. The applied field gives rise to a flexoelectric torque, which varies linearly with the field. This produces a twist (ϕ) distortion of the director without any threshold, resulting in $-oscillations at the frequency of the applied field. This in turn gives rise to the f component of the optical signal in the transmitted light.

We have developed a simplified model for the electrooptic response of the system, from which we can estimate the anchoring energy for azimuthal orientation of the nematic director at the two surfaces of the cell. Our measurements on PCH-7 lead to the following results:

a) Oblique coating of SiO to get zero pretilt angle of the nematic director at both the walls does not produce any f signal, as can be expected.

b) If the angle of oblique coating of SiO is such that a large pretilt angle (—0.35 radians) is produced at one plate and zero pretilt angle at the other plate, we get an f signal which increases linearly with the applied field. The f signal decreases steeply with the frequency of the applied field (Fig.7). The theoretical calculations made by assuming strong anchoring at the two surfaces of the cell broadly agreed with the experimental values. The SiO coating appears to result in strong anchoring for azimuthal orientation.

c) If one plate is coated with SiO vapour to get zero pretilt angle and the other plate is coated with polyimide and unidirectionally rubbed to get a small pretilt angle (0.035 radians) we get a relatively small f signal. Calculations made by assuming strong anchoring at both the plates do not match with the experimental data. We have to assume that the anchoring is weak at the polyimide coated surface to explain the observations.

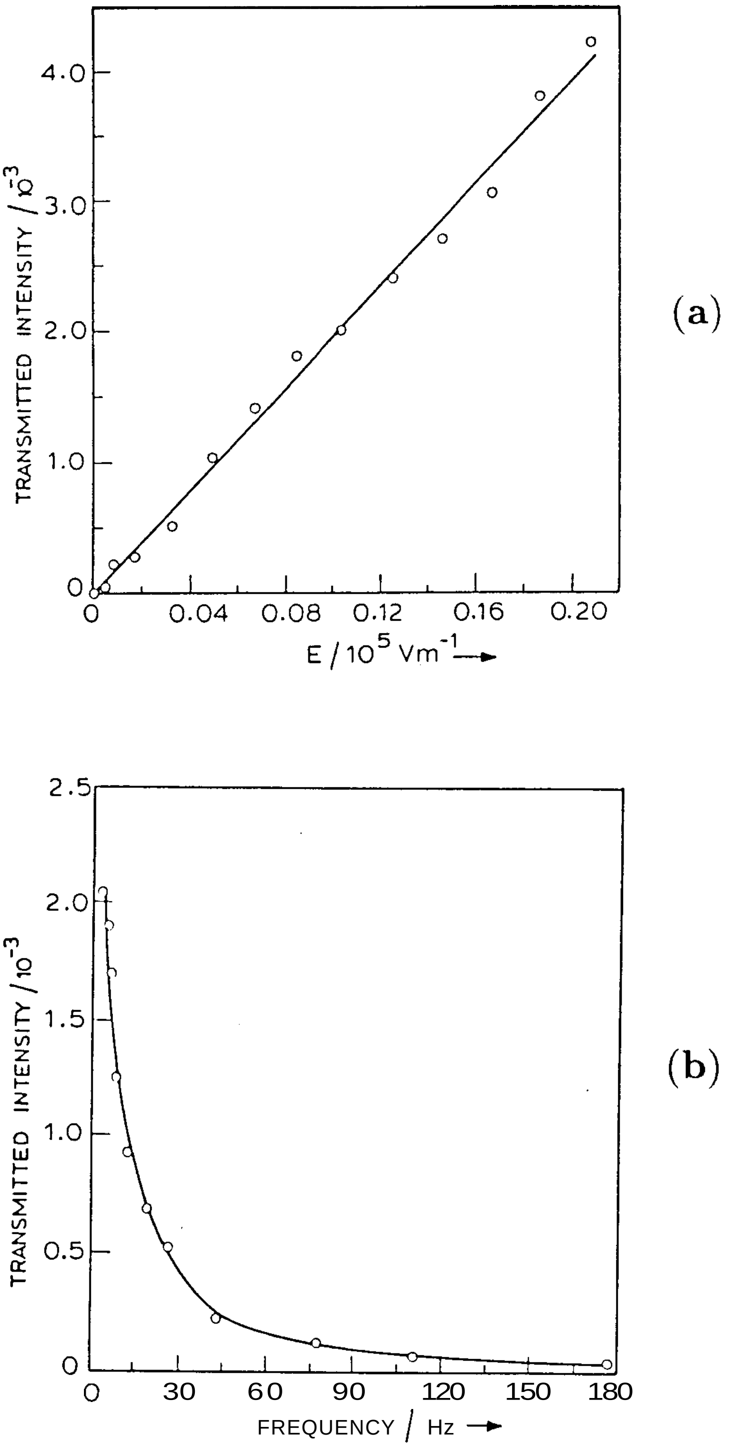

Fig.7: (a) Field dependence of the f component of transmitted intensity for a cell with a large splay distortion at a temperature of 313 K. Frequency of the applied field = 7 Hz. Sample thickness = 24.2 μm. (b) Frequency dependence of the f component of transmitted intensity at E = $0.083 \times 10^5 V/m$ at a temperature of 313 K.

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1. Propagating electroconvection in nematic liquid crystals under *DC* excitation.
   (V.A.Raghunathan, P.R.Maheswara Murthy and N.*V.Madhusudana)*
   Current Science, 59, (1990)

2. Propagating electrohydrodynamic instabilities in nematics.
   (V.A.Raghunathan, P.R. *Maheswara* Murthy and N.V. Madhusudana)
   Mol. Cryst. Liquid Cryst., 199, 239-248 (1991).

3. *Flexoelectric coefficients* of some nematic liquid crystals.
   (P.R.Maheswara Murthy, *V.A.Raghunathan* and N.*V.Madhusudana)*
   Proceedings of the Solid State Physics Symposium, 1991,
   Banaras Hindu University, Varanasi, Vol. *34C,* 357.

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   (V.A.Raghunathan, P.R.Maheswara Murthy and N.V. Madhusudana)
   Pattern formation in complex dissipative system, Ed. S. Kai
   (World Scientific Pub. Co., Singapore, *1992),* p.255.

5. An AC electrooptic technique of comparing the two anchoring energies of a hybrid aligned nematic cell.
   (P.R.Maheswara Murthy, *V.A.Raghunathan* and N.V. Madhusudana)
   Liquid Crystals **14,** 1107 (1993).

6. Experimental determination of the *flexoelectric* coefficients of a number of nematogens.
   (P.R.Maheswara Murthy, V.A.Raghunathan and N.V. Madhusudana)
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