Chapter 7

MAGNETIC SUSCEPTIBILITY MEASUREMENTS

7.1   Introduction

As mentioned in the previous chapters we have related some of the dielectric and optical measurements to the orientational order parameter which was determined using magnetic susceptibility measurements. In this chapter **we** will describe the magnetic susceptibility measurements. We can measure the orientational order parameter by using the anisotropy of any appropriate physical property of the medium. For example optical, dielectric or diamagnetic anisotropies can be used for this purpose [1]. The dielectric constant is ≥ 4 in typical cases and the local field correction is substantial. Further, in an anisotropic medium a calculation of the internal field is quite difficult. Also as we have discussed earlier, the short range order can vary with temperature making an absolute measurement of the order parameter difficult using the dielectric data. On the other hand the diamagnetic susceptibility is very small ($\sim 10^{-7}$ cgs units per gram) and hence internal field effects can be neglected. For this **reason** the diamagnetic anisotropy is extensively used to measure the orientational order parameter of nematic liquid crystals [3,74,106-109].

The diamagnetic susceptibility $\chi_{\alpha\beta}$ relates the induced magnetic moment $\vec{M}$ (per unit mass), to the applied field $\vec{H}$:

$$M_\alpha = \chi_{\alpha\beta}H_\beta; \quad \alpha, \beta = x, y, z \tag{7.1}$$

where $\chi_{\alpha\beta}$ denotes an element of the susceptibility tensor χ. Choosing the **z-axis along** the director, the tensor corresponding to the nematic phase is given by

$$\chi = \begin{pmatrix} \chi_\perp & 0 & 0 \\ 0 & \chi_\perp & 0 \\ 0 & 0 & \chi_\| \end{pmatrix} \tag{7.2}$$

where the subscripts $\|$ and $\perp$ refer to the directions parallel and perpendicular to the director, respectively. The average mass susceptibility is given by

$$\bar{\chi} = \frac{1}{3}\sum_\gamma \chi_{\gamma\gamma} = \frac{1}{3}(\chi_\| + 2\chi_\perp) \tag{7.3}$$

In the isotropic phase $\chi_{\alpha\beta} = \chi\delta_{\alpha\beta}$.

The average mass susceptibility is independent of **temperature, i.e.** $\bar{\chi}$ in the nematic phase is equal to the isotropic phase susceptibility. The **magnetic anisotropy** is defined as

$$\chi_a = \chi_\| - \chi_\perp = \frac{3}{2}(\chi_\| - \bar{\chi}). \tag{7.4}$$

The order parameter is then

$$S = \frac{\chi_a}{\Delta\chi_0} \tag{7.5}$$

where $\Delta\chi_o$ is the diamagnetic anisotropy in the fully aligned state i.e. for $S = 1$. In Section 7.3 we describe a method of calculating $\Delta\chi_o$.

7.2 Experimental

The magnetic susceptibility is measured by the classical Faraday-Curie method. A schematic diagram of the experimental setup is shown in Figure 7.1. The sample is placed in a magnetic field that has a gradient in the vertical direction and the force acting on the sample is determined by using a sensitive balance. The energy (U) of a sample of mass **m** and magnetic susceptibility χ when kept in horizontal magnetic field H_x is given by

$$U = -\frac{m\chi H_x^2}{2} \tag{7.6}$$

The vertical force F_z exerted on this sample is then given by

$$F_z = m\chi \left(H_x \frac{\partial H_x}{\partial z} \right) \tag{7.7}$$

$F_z = \Delta mg$ where **Am** is the extra mass measured by the balance due to the force exerted by the field gradient, and g is the acceleration due to gravity. As in all the samples we have used $\chi_a > 0$, the field causes a uniform orientation of the director along the direction of the field, and $\chi_\parallel$ can be measured. A measurement of χ in the isotropic phase gives the value of $\bar{\chi}$ and hence S (see Equations 7.4 and 7.5).

7.2.1 Description of the Apparatus and Procedure

An OXFORD INSTRUMENTS N100 electromagnet with Faraday pole tips has been used to conduct the experiments [110, 111]. The pole tips are shaped to give a region where $(H_x \frac{dH_x}{dz})$ is constant. This region is approximately 15mm high and 12mm wide. The force is measured by a Sartorious balance model S3DV with a digital control unit, which has a maximum capacity of 3 **g** and sensitivity of 0.1 μg (Figure 7.1). Using two translational stages the balance beam may be shifted approximately 5mm in the $\pm$ **x,** $\pm$ y directions to adjust the position of the sample.

The sample is loaded in a variable temperature continuous flow cryostat CF 1200 (OXFORD INSTRUMENTS). It is top loaded through an access port on top of the cryostat. This port is sealed by a plug against an 'O' ring and the sample is suspended through this port by a quartz fibre and hung onto one side of the balance. After the sample is loaded, compensating weights are added to the pan on the other side so that the reading on the balance is close to 0. The cryostat is then evacuated by a rotary pump. To improve the heat flow in the sample chamber after evacuating it, it is filled with helium as a heat exchange gas.

The quartz fibre has a diameter of ~ 124 μm. The advantage of using quartz fibre is that its susceptibility and the temperature variation of the susceptibility are low. Hence it can be used over a wide range of temperatures. The length of the fibre ($\sim$62 cm) is adjusted so that the sample when suspended is very close to the heater. The sample cup is held in an aluminium pan and is suspended at the end of the quartz fibre. The vertical '**z**' position of the heater is adjusted so that the field gradient at the sample **and** hence the force measured is maximum. At the bottom of the sample chamber, just above the heater, there is a beta **lamp** which illuminates the sample. With the aid of this beta **lamp** we can see that the sample is centred properly.
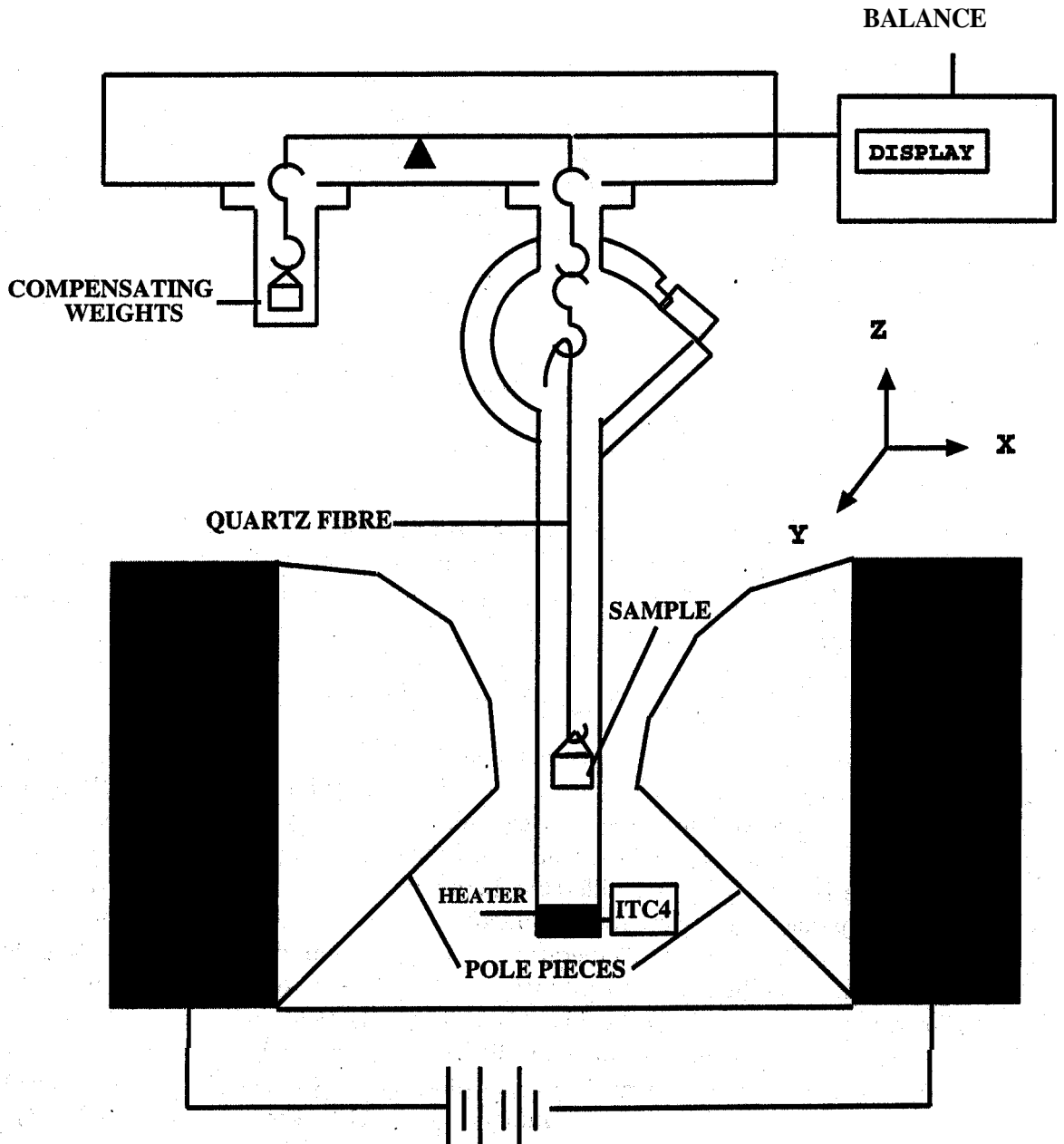
Figure 7.1: Schematic diagram of the experimental setup used to conduct the magnetic susceptibility measurements.
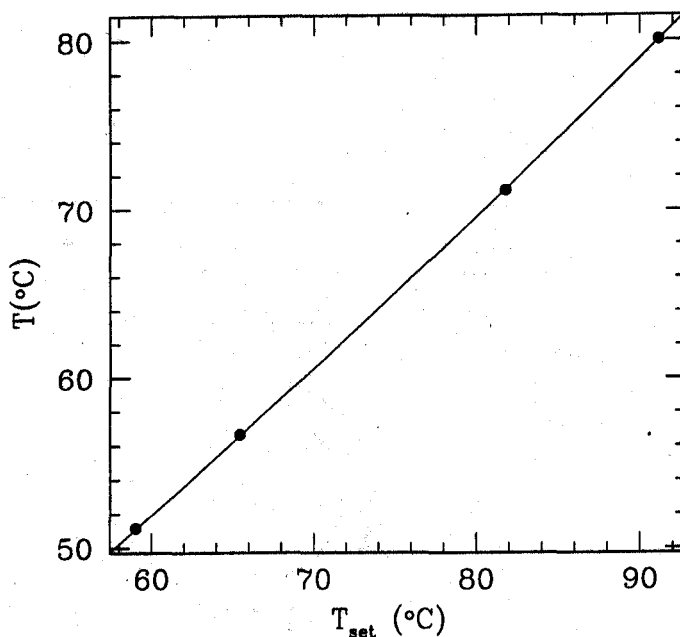
Figure 7.2: Temperature calibration curve of the sample area as a function of the temperature set on the ITC4. The line corresponds to the fit $T = 230.011 - 0.2793(T_{set} + 273.15) + 0.001695(T_{set} + 273.15)^2 - 273.15°C$. Where T is the sample area temperature and T_{set} is the temperature set on the ITC4.

7.2.2 Temperature and Field Gradient Calibration

The temperature of the sample region is controlled by an OXFORD INSTRUMENTS Intelligent Temperature Controller (ITC4). The sensor is a Chromel-alumel thermocouple positioned at the bottom of the crysostat near the heating coil. The temperature can be set to an accuracy of 0.1 K. As the sensor is slightly below the sample and the sample is not in direct contact with the heater there is a temperature difference between that of the sample and the temperature set an the front panel of the temperature controller. To calibrate the temperature of the sample we have used the N-I transition temperatures of the compounds for which we have measured the magnetic susceptibility as the calibration points. We have fitted a polynomial to these calibration points as shown in Figure 7.2. To calibrate the field gradient we have measured the force experienced by a standard sample, for different dial settings on the magnet power supply. The sample used was mercury tetrathiocyanatocobaltate $(HgCo(CNS)_4)$ which is known to have a mass susceptibility of 16.44×10^{-6} cgs units st 20° C [112]. Figure 7.3 shows the $H_x \frac{dH_x}{dz}$ as a function of the dial setting on the power supply. For most of the experiments we have used a $H_x \frac{dH_x}{dz}$ of $\sim 10^7$ gauss^2/cm.

7.2.3 Sample Preparation

To reduce the amount of sample required for the susceptibility measurement the sample has been taken in aluminium cups usually used with the Perkin Elmer DSC. The mass of the cup is ~ 30 mg, whereas that of the quartz ampoule which is usually used in such experiments is much larger (0.5 gm) . Another advantage of using aluminium cups is that the sample temperature can be expected to be more uniform and temperature stability is also obtained in a shorter time (~ 10
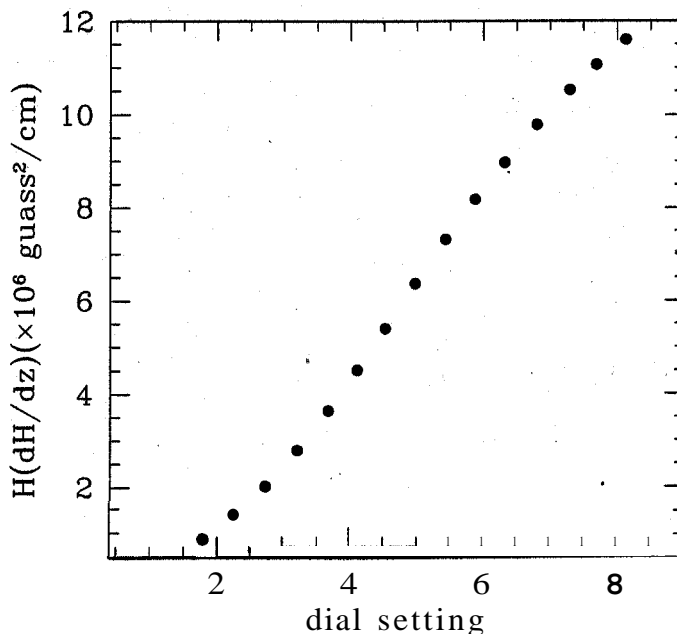
Figure 7.3: Calibration points for $H_x \frac{dH_x}{dz}$ as a function of the dial setting on the power supply.

min) than in a quartz ampoule ($\sim$ 20 to 30 min at about 70°C). The total mass of the aluminium cup and the sample is $\sim$ 50 mg. The cups are pressure sealed. As the samples are liquid when heated they tend to leak from the rims of these cups even after pressure sealing. To prevent this leakage the cups are further sealed with a silicone rubber adhesive. The susceptibilities of both the aluminium cup and the silicone rubber adhesive have been measured as functions of temperature and ultimately their contributions have been subtracted from the total **Am** experienced by the sample cups. Figures 7.4 and 7.5 show the variations of the **Am** experienced by an aluminium cup and silicon rubber adhesive as functions of temperature. **42.1mg** of the silicone rubber adhesive was used in the measurement while 3 to 4 mg are typically needed to seal the aluminium cup.

7.3 Results

We have measured the magnetic susceptibility of the following compounds: p-cyanophenyl p-n heptylbenzoate (CP7B), octyloxy cyanobiphenyl(8OCB) 5-n-heptyl-2(4-cyanophenyl)-pyrimidine (ROCP7037) and 4methoxyphenyl-trans -4-pentyl cyclohexylcarboxylate (S1495). The chemical structures and their transition temperatures are shown in Figure 7.6. The magnetic susceptibility of ROCP7037 and CP7B have been measured previously by Buka and de Jeu [74]. Our values are $\sim$ 8% less than their values.

All the measurements were made by cooling the sample in steps of 0.1 to 5°C depending on the proximity to the N-I transition point. After the set temperature was reached it was allowed to stabilise for $\sim$ 10 to 15 minutes. The temperature stability was reflected in the stability of the **Am** measurement. As can be seen from Equation 7.7 the mass susceptibility χ of the sample is given by

$$\chi = \frac{\Delta m_{sample} \times 980}{m_s (H_x \frac{dH_x}{dz})} \text{ cgs units} \tag{7.8}$$
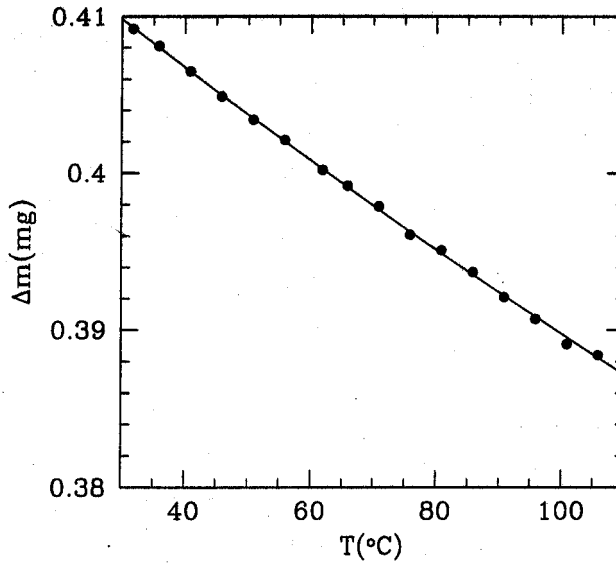
Figure 7.4: Variation of *Am* for an aluminium cup of mass 56.1 mg as a function of temperature. The fit corresponds to $Am = 0.536366 - 5.237976 \times 10^{-4}(T + 273.15) + 3.508352 \times 10^{-7}(T + 273.15)^2$. $H_x dH_x/dz = 1.18 \times 10^7$ gauss ^{2}/cm.
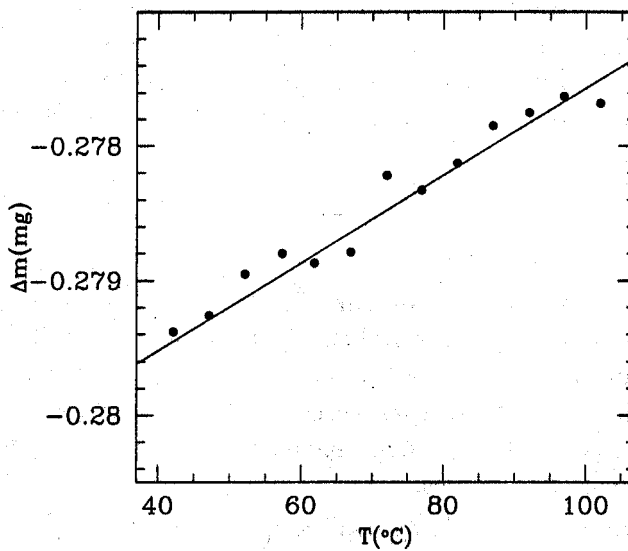

Figure 7.5: Variation of *Am* of silicon rubber adhesive of mass 42.1mg as a function of temperature. The fit corresponds to $Am = -0.28971329 + 3.25465 \times 10^{-5}(T + 273.15)$. $H_x dH_x/dz = 1.18 \times 10^7$ gauss^2/cm.
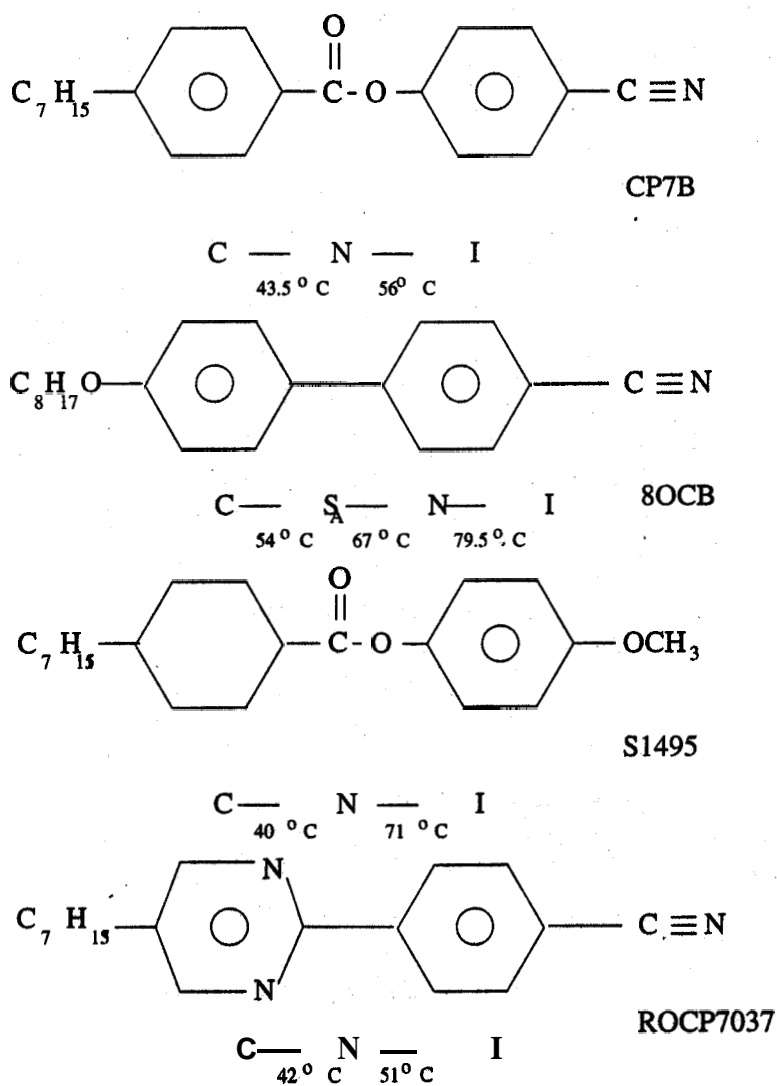
Figure 7.6: Chemical structures and transition temperatures of the compounds used in the experiments reported in this chapter.
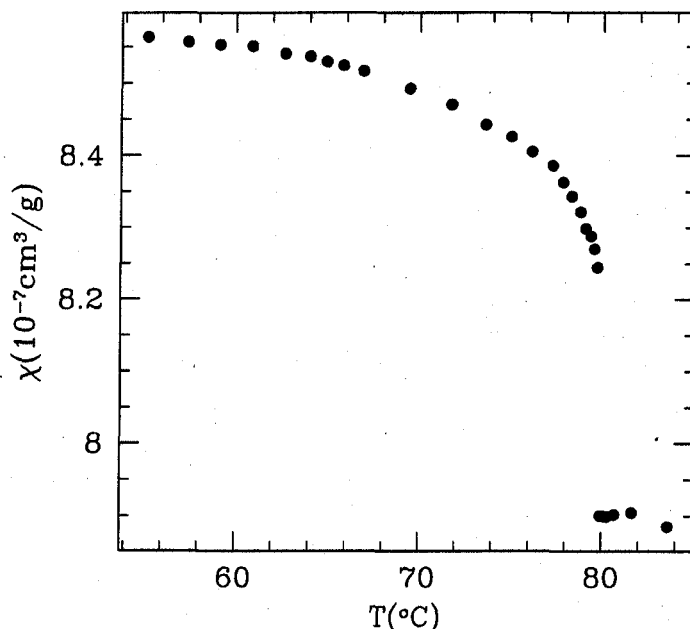
Figure **7.7**: Variation of χ of 8OCB as a function of temperature.

where **A m** is the extra mass measured by the balance due to the force experienced by the sample of mass m_s for a field gradient of $H\frac{dH}{dz}$. In the isotropic phase $\chi = \bar{\chi}$ whereas in the nematic phase $\chi = \chi_{\|}$. For all the measurements we have used $H_x dH_x/dz = 1.18 \times 10^7$ gauss^2/cm.

Figures **7.7, 7.8, 7.9** and **7.10** show the temperature variations of χ as functions of temperature of the compounds mentioned above. $\Delta\chi_o$ can be calculated by using the Haller extrapolation technique [113]. **Haller** et *al* [113] made a log-log plot of the scaled polarizability vs reduced temperature to get a straight line. They extrapolated this straight line to 0 K to obtain the anisotropy of the polarisability in the fully aligned state. Using this they calculated the absolute order parameter. This technique has been used by many authors to calculate the absolute order parameter [74, 108]. To calculate $\Delta\chi_o$ we have fitted the experimentally measured χ_a to the form

$$\chi_a = \Delta\chi_o \left(1 - \frac{yT}{T_{NI}}\right)^z \tag{7.9}$$

where **AX,,** y and z are fit parameters and T is in K. From the fitted $\Delta\chi_o$ we calculate the order parameter S as

$$S = \frac{\chi_a}{\Delta\chi_o} \tag{7.10}$$

Figures **7.11, 7.12, 7.13** and **7.14** show the graphs of the experimental data fitted to the functional form given in Equation **7.9.** For fitting the parameters we used the software **COPLOT**.
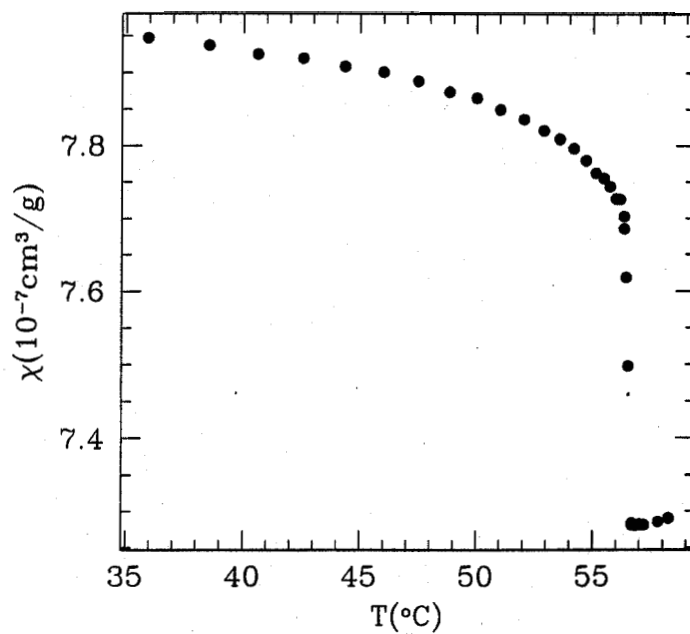
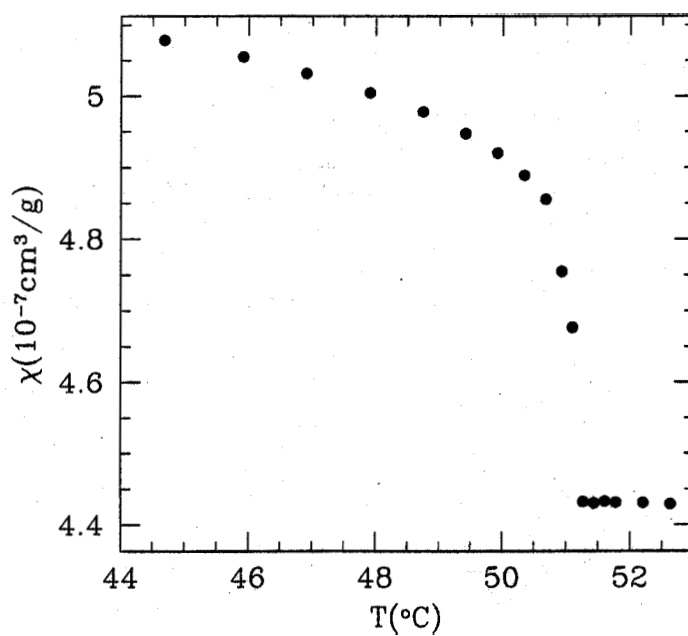**Figure 7.8: Variation of χ of CP7B as a function of temperature.**

Figure 7.9: Variation of χ of ROCP7037 as a function of temperature.
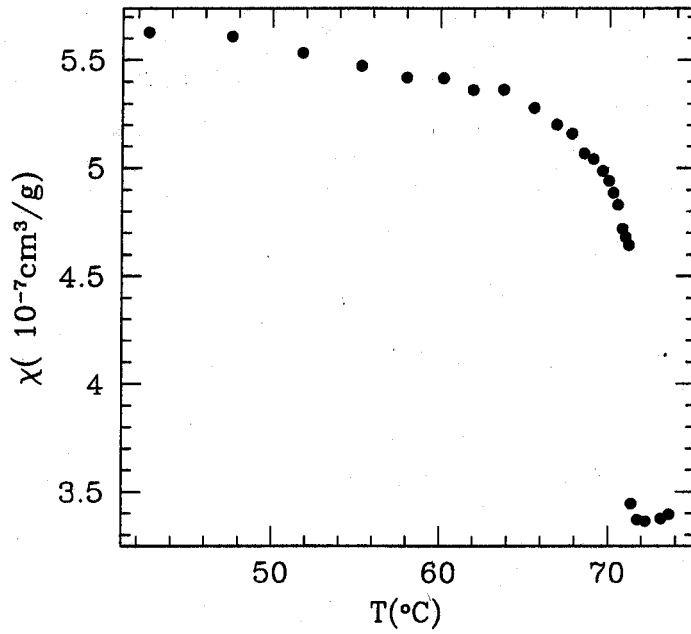
Figure 7.10: Variation of χ of S1495 as a function of temperature.

Figure 7.11: Theoretical fit of χ_a to the functional form shown in Equation 7.9 for 8OCB. Data calculated from that shown in Figure 7.7.

Figure 7.12: Theoretical fit of χ_a to the functional form shown in Equation 7.9 for **CP7B**. Data calculated from that shown in Figure 7.8.

Figure 7.13: Theoretical fit of χ_a to the functional form shown in Equation 7.9 for **ROCP7O37**. Data calculated from that shown in Figure 7.9.
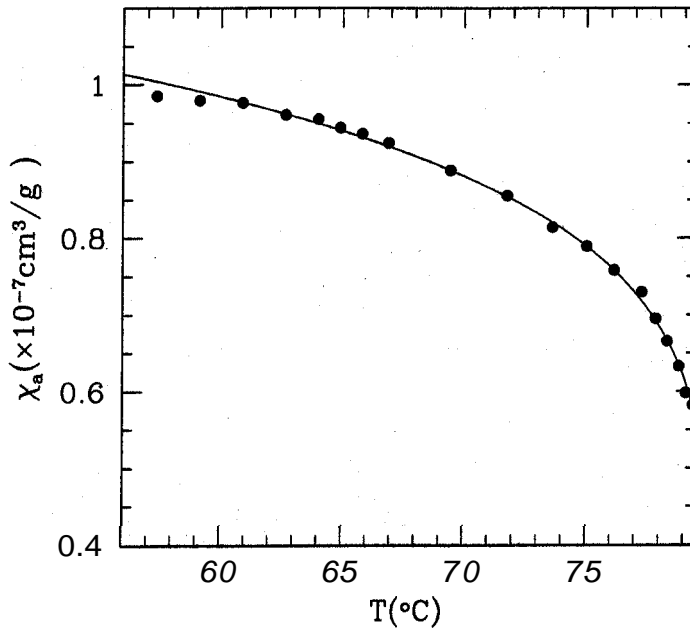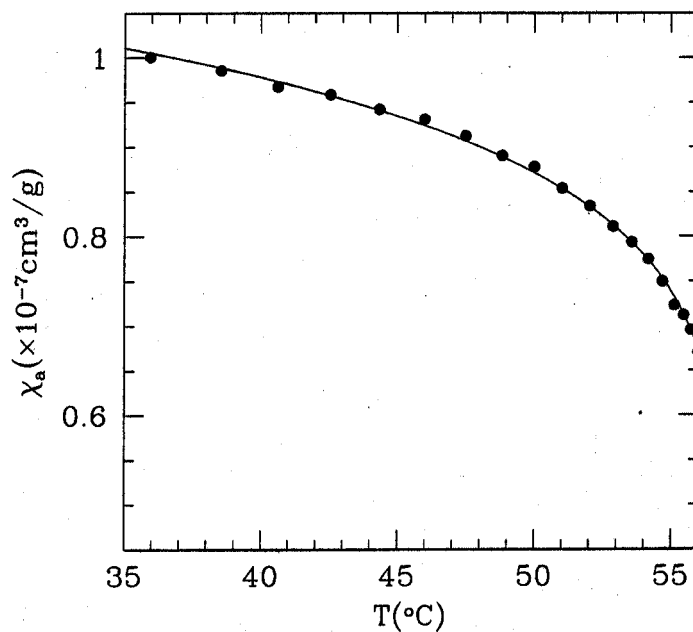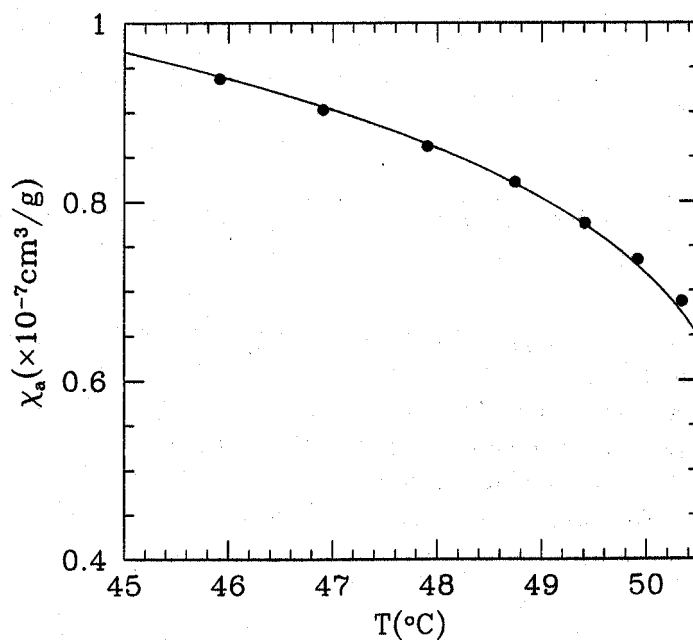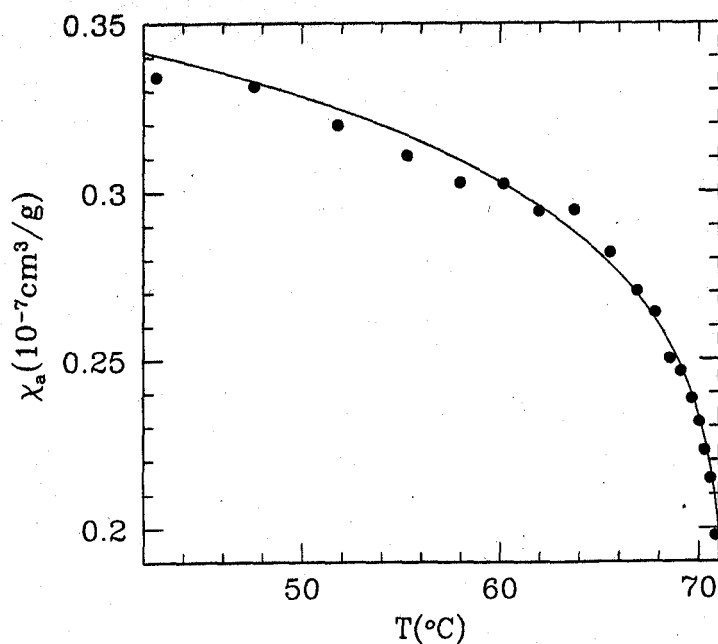
Figure **7.14:** Theoretical fit of χ_a to the functional form shown in Equation **7.9** for S1495. Data calculated from that shown in Figure **7.10.**

Sample	$T_{NI}(°C)$	$\Delta\chi_o$ (10^{-7} cgs units)	y .	z
80CB	**79.5**	**1.56**	**0.9882**	**0.162**
CP7B	**56.0**	**1.44**	**0.9887**	**0.130**
ROCP7037	**51.0**	**1.94**	**0.9976**	**0.175**
S1495	**71.0**	**0.462**	**0.9944**	**0.126**

Table **7.1:** Fit parameters for the different compounds according to the functional form given in Equation **7.9.**

Figure **7.15** shows the order parameters calculated from Equation **7.10** for all the compounds. Table **7.1** shows the clearing temperatures and the fitting parameters for the compounds used in this chapter.

It should be noted that T_{NI}/y is the temperature at which the order parameter calculated using the functional form shown in Equation **7.9** goes to zero. According to the y values shown in Table **7.1,** this value occurs at $\sim$ **2** to **3°C** above T_{NI} showing that the N-I transition is really a weak first order transition. The values of y and z are similar to those obtained by Buka and de Jeu [74]. As discussed **by** them, the low values of z (< 0.18) indicate that the order parameter has a much slower variation with temperature than implied by the mean field models, as we have discussed in Chapter **3.**
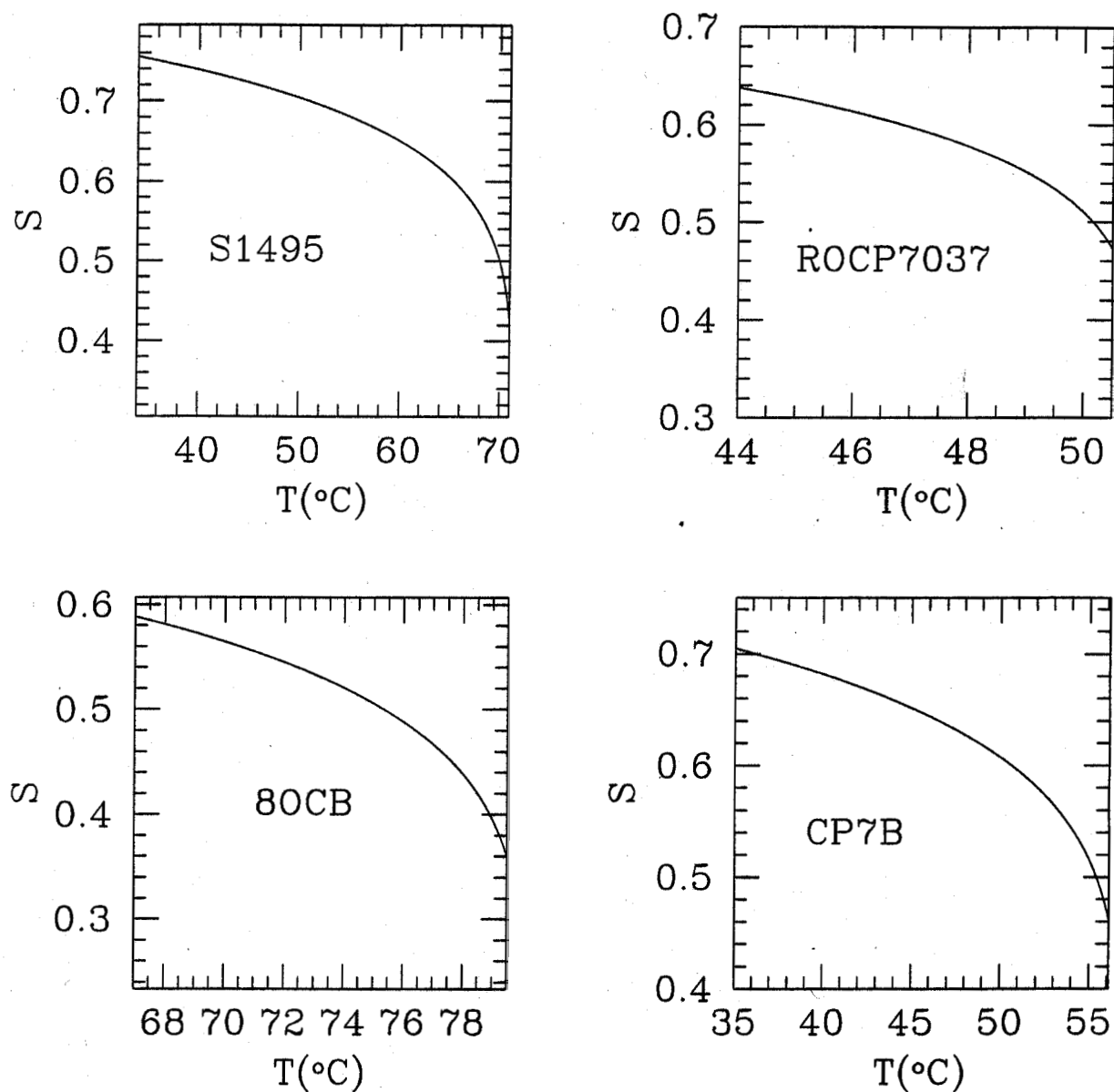
Figure 7.15: Order parameter as calculated according to Equation 7.10 for all the compounds.

SUMMARY

In this thesis we have described a new experimental technique for conducting quantitative electrical and optical measurements on liquid crystals under the application of a strong electric field. We have shown that even small heating effects ($< 0.01°C$) can be measured with an in **situ** nickel resistance thermometer. We have studied the field effect on the nematic-isotropic and nematic-smectic A phase transitions in a few highly polar compounds. In ,principle this technique can be used to study the effect of a strong electric field on any liquid crystalline system.

Using dielectric measurements we have probed the paranematic-nematic critical region in **5CB** and **8OCB**. We have fitted the experimental results to an appropriate Landau theory and obtained the corresponding Landau coefficients. The Landau parameters for **5CB** broadly agree with previous measurements.

We have presented the first experimental results of the effect of a strong electric field on the N-S_A phase transition in a pure compound (**8OCB**) to find that the transition **temperature** shows a quadratic dependence on the applied electric field. This is consistent with the prediction of the relevant Landau theory. We have seen that both the N-S_A and the S_A-N_R transition temperatures in a mixture exhibiting the reentrant nematic phase increase with field. The former increases less rapidly than the latter indicating that the S_A phase maybe bounded above at a high enough electric field, though we could not reach such a field in our experiments.

We have found experimental evidence for *polar short range order* in a nematogen which has a large positive dielectric anisotropy (**CP7B**). The compound exhibits a large enhancement of the order parameter under the application of a strong electric field. The divergence of the second and third harmonic electrical signals indicate that we can reach the critical region in our experiments. We have presented the first measurements on the conductivity of a nematogen under a strong electric field near the paranematic-nematic critical point. We have discussed the variation of the conductivity in the nematic phase in terms of the combined effects of the ionic conductivity, and a molecular relaxation. These in turn **vary** with the orientational order parameter which depends on field and temperature. We interpret the peak in the conductivity near the **paranematic**-nematic critical point to be due to the critical slowing down of polar domains. The detection of a small but significant second harmonic signal supports this interpretation. These experimental studies may indicate one possible route to the realisation of a polar nematic liquid crystal.

The experimental results on a mixture exhibiting the reentrant nematic phase and CP7B indicate that as the temperature is lowered the concentration of molecules in the parallel configuration increases. This supports the molecular model developed by our coworkers which **was** initially put forward to explain the phenomenon of double reentrance.

We have conducted low frequency electrooptic measurements which show the direct influence of the electrolytic nature on the electrooptic response of the nematic liquid crystals subjected to strong electric fields. We have discussed a possible origin of the optical response to be due to the coupling of flexoelectric polarisation with the field gradient in the sample. Further

experimentation and theoretical modeling is required to understand the mechanisms involved in this process.

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