

CHAPTER V

SURFACE TENSION OF SMECTIC LIQUID CRYSTALS

After the early efforts of **Jaeger**¹ in 1917, who measured the surface **tension** of **e-p-azoxybenzoate** by the maximum bubble pressure method, there have been no other systematic measurements of surface **tension in** the smectic phase. **Schwartz** and **Moseley**² who used the ring method failed to **make** any measurement in the smectic phase due to its high viscosity. More recently **Churchill and Bailey**³ and **Gannon and Faber**⁴ also report that they were unable to get reproducible results in the smectic phase. **So** the results reported here appear to establish the superiority of the pendant drop method in dealing with highly viscous **and** anisotropic liquids.

The γ -**T** characteristics of two smectogenic compounds were studied:

1. n-p-Cyanobenzylidene-p-n-octyloxyaniline
(CBOOA)
2. ethyl p-azoxybenzoate.

Both the compounds were purified by several recrystallisations using suitable solvents. The γ -T curves obtained for these compounds are discussed here.

CBOOA

This compound exhibits the smectic A and nematic phases before going over to the isotropic phase. The transition temperatures of the sample used were: solid-smectic A 75°C , smectic A - nematic 83.2°C and nematic-isotropic 107°C . The structural formula of this compound is given in fig.5.1. The values of γ and ρ are tabulated in Tables 5.1 and 5.2. The density data are due to Price.⁵ Experiments were repeated twice with fresh samples and similar γ -T curves were obtained with the values of γ agreeing to within 1%.

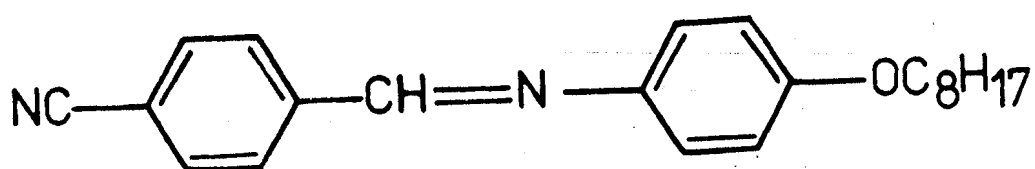


Figure 5.1

Structural **formula** of n-p-cyanobenzylidene -
p-n-octyloxyaniline

The γ -T curve in this case (fig.5.2) exhibits a positive slope throughout the smectic phase, At the smectic A - nematic transition, the slope changes sign with γ assuming a monotonic decreasing trend. Throughout the nematic phase the slope has a small negative value. At the N-I transition, the slope again becomes positive and remains so, for a range of about 4°C in the isotropic phase, The slope then changes sign and γ shows a monotonic decreasing trend as in the case of other systems.

The γ -T characteristic of this compound was studied earlier, though only in the nematic phase, by Langevin⁶ who has reported that γ decreases with temperature with a small temperature gradient. This observation is in agreement with ours. Later in 1979 Sohl et al⁷ studied the γ -T characteristic of this compound by the capillary waves method. The curve obtained by them is shown in fig.5.3. Except for the initial negative trend in their curve, the

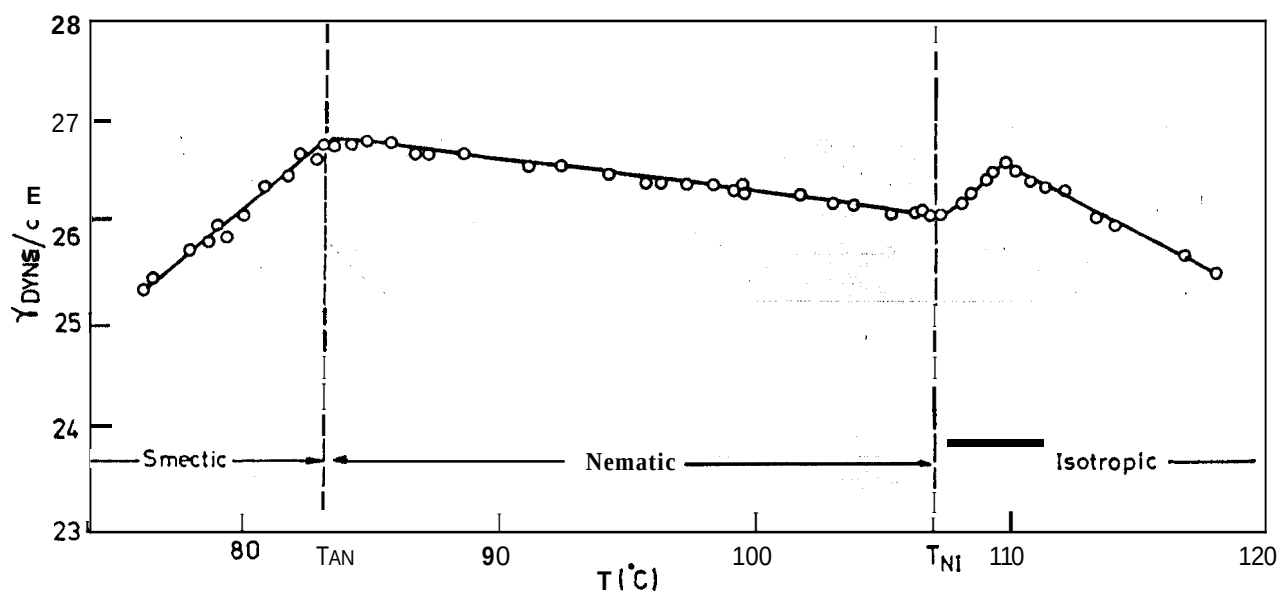


Figure 5.2

Surface tension-temperature characteristic **curve** for CBOOA
(**Present** investigations).

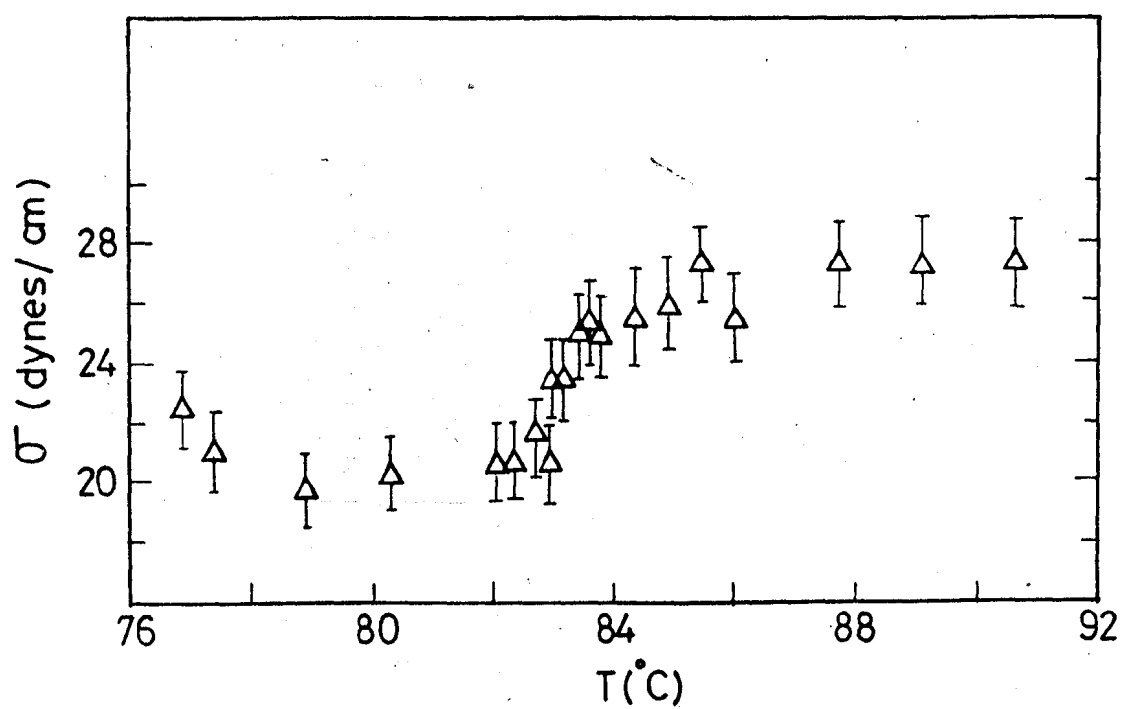


Figure 5.3

Surface **tension**-temperature characteristic curve for CBOOA (After Sohl et al.⁷).

behaviour is similar to **that** of ours in the smectic phase. In the nematic phase they find almost a steady value of γ , but their range of measurement in **this phase is** only up to about 91°C . They **would** probably have observed the small negative slope if they had extended their measurements up to the NI transition (about 107°C). The error bars are rather large in their measurements.

In the smectic **phase, we** can expect a sharp density discontinuity at the surface resulting in a strong surface **field which** in turn produces **an** enhanced **surface excess** order. The theory **predicts**⁸ a positive slope throughout the smectic phase, which is in good agreement with our result here. **Again,** the positive slope in the isotropic phase indicates a surface excess order in the isotropic phase.

Ethyl-p-azoxybenzoate

This compound **shows** the **smectic** A and isotropic phases. The **A-I** transition temperature of the sample used was **166.6°C**. The structural formula is given in **fig.5.4**. Experiments were repeated three times in this **case** using fresh samples and the values agreed to within 1%. Tables 5.3 and 5.4 give the **values of γ and ρ at different temperatures**. The density data are due to Jaeger.¹

The γ -T curve of **this** compound is shown in **fig.5.5**. As we can see, the slope is positive in the **smectic** phase with a very steep rise in the value of γ as the **A-I** transition point is approached. At **T_{A-I}**, the slope changes **sign** initially with γ showing a decreasing trend. But very soon it starts increasing with the slope becoming positive **again**. It remains positive **over** a wide temperature range of about **30°C** and then **changes** sign, γ showing a

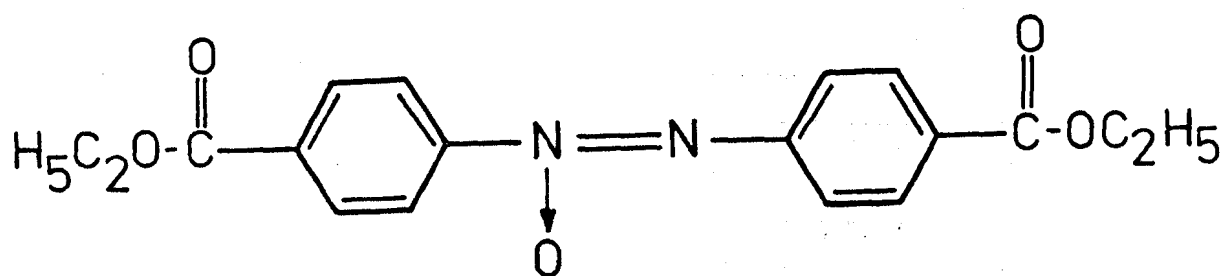


Figure 5.4

Structural formula of ethyl p-azoxybenzoate

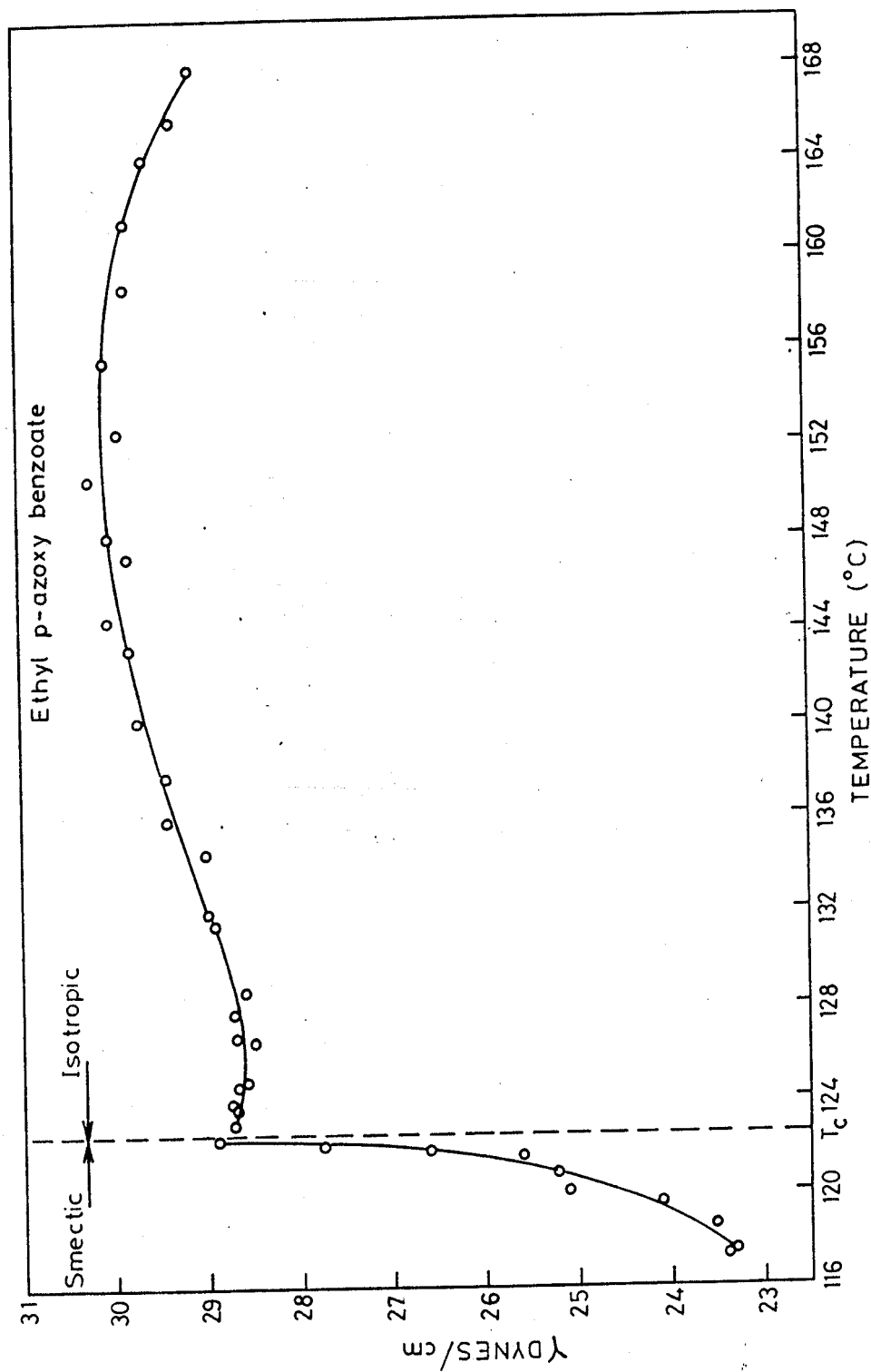


Figure 5.5

Surface tension-temperature characteristic curve for ethyl p-azoxybenzoate (present investigations).

monotonic decreasing trend thereafter.

There have been two earlier measurements^{1,2} of γ of this compound as a function of temperature. The γ -T curves are reproduced in fig.5.6. The two curves are in total disagreement in the isotropic phase. In the smectic phase, Schwartz; and Moseley could not make any measurement. In the isotropic phase their curve shows a positive slope over a wide range of temperature. Jaeger's curve shows a sudden increase in the value of γ just before the A-I transition, with only one point to show the rise. In the isotropic phase the value of γ drops down very quickly and remains constant up to a range of 50° and then shows a hump which appears to be inconsistent. The curve obtained by Schwartz and Moseley in the isotropic phase is closely similar to ours.

A comparison of the γ -T curve of this compound with that of CB00A appears to be interesting. In

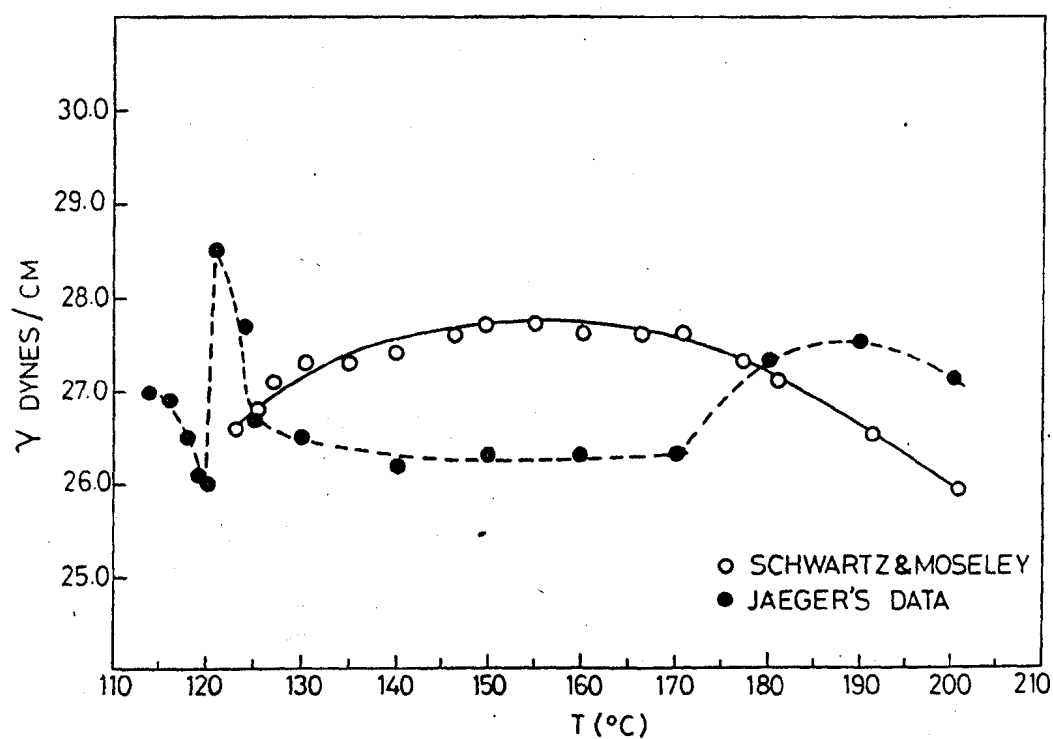


Figure 5.6

Surface tension-temperature characteristic curve
for ethyl p-azoxybenzoate. (After references 1,2).

the case of CB00A, the smectic A phase transform to the nematic phase whereas in this case the smectic A phase **transforms** to the isotropic phase. Hence the excess surface order in this case may be expected to be more than that in the case of CB00A. **This** is probably the reason for the steep rise in the value of γ with a very large value of the slope $d\gamma/dT$. Similarly the continuation of the smectic order at the **surface** in the isotropic phase ~~may~~ be responsible for a prolonged positive slope in the isotropic phase. **This** is in agreement with the results of **Nielsen et al**⁹ who have found the **smectic** order in the isotropic phase of a smectic liquid crystal by Xray methods.

In summary, therefore, we present in this chapter the first reliable measurement⁸ of γ for the smectic A phase under thermodynamic equilibrium conditions. **The** data indicate an excess surface order throughout the smectic phase and over a certain

range of temperature in the isotropic phase also. The results are in conformity with the theoretical expectations.

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Table 5.1

Surface Tension of CBOOA

Temperature °C	γ dyne cm ⁻¹	Temperature °C	dyne cm ⁻¹
76.0	25.4	98.3	26.4
76.4	25.5	99.2	26.3
77.8	25.8	99.4	26.4
78.6	25.9	99.5	26.3
79.0	26.0	101.7	26.3
79.4	25.9	103.0	26.2
80.0	26.1	103.8	26.2
80.7	26.4	105.1	26.1
81.7	26.5	106.1	26.1
82.2	26.7	106.4	26.1
82.8	26.7	106.6	26.1
83.1	26.8	107.3	26.1
83.4	26.8	108.0	26.2
83.7	26.9	108.3	26.3
84.2	26.8	109.0	26.4
84.7	26.8	109.2	26.5
85.8	26.8	109.7	26.6
86.6	26.7	110.1	26.5
87.1	26.7	110.7	26.4
88.7	26.7	111.3	26.4
91.1	26.6	112.1	26.3
92.5	26.6	113.3	26.1
94.2	26.5	114.0	26.0
95.6	26.4	116.8	25.7
96.2	26.4	117.9	25.5
97.2	26.4		

Table 5.2

Density of CBOOA

Temperature °C	Density gm/cc	Temperature °C	Density gm/cc
76.0	0.9491	98.3	0.9339
76.4	0.9453	99.2	0.9329
77.8	0.9446	99.4	0.9327
78.6	0.9441	99.5	0.9326
79.0	0.9439	101.7	0.9311
79.4	0.9437	103.0	0.9302
80.0	0.9434	103.8	0.9297
80.7	0.9430	105.1	0.9287
81.7	0.9425	106.1	0.9273
82.2	0.9422	106.4	0.9278
82.8	0.9419	106.6	0.9269
83.1	0.9417	107.3	0.9264
83.4	0.9416	108.0	0.9258
83.7	0.9414	108.3	0.9254
84.2	0.9412	109.0	0.9248
84.7	0.9409	109.2	0.9246
85.8	0.9403	109.7	0.9242
86.6	0.9399	110.1	0.9238
87.1	0.9396	110.7	0.9233
88.7	0.9388	111.3	0.9228
91.1	0.9375	112.1	0.9221
92.5	0.9416	113.3	0.9210
94.2	0.9359	114.0	0.9204
95.6	0.9351	116.8	0.9180
96.2	0.9348	117.9	0.9170
97.2	0.9330		

Table 5.3**Surface tension of ethyl p-azoxybenzoate**

Temperature °C	γ dyne cm ⁻¹	Temperature °C	γ dyne cm ⁻¹
117.2	23.4	128.5	28.6
117.5	23.3	131.3	28.9
118.5	23.5	131.8	29.0
119.6	24.1	134.4	29.0
120.0	25.1	135.8	29.4
120.8	25.2	137.6	29.4
121.6	25.6	140.2	29.7
121.8	26.6	143.2	29.8
122.1	27.8	144.4	30.0
122.3	28.9	147.3	29.8
122.8	28.7	148.1	30.0
123.6	28.7	150.5	30.2
123.7	28.7	152.5	29.9
124.4	28.6	155.5	30.0
124.5	28.7	158.7	29.8
126.5	28.7	161.4	29.8
127.6	28.7	164.2	29.6
		165.6	29.3
		167.8	29.1

Table 54

Density of ethyl p-azoxybenzoate

Temperature °C	Density gm/cc	Temperature °C	Density gm/cc
117.2	1.1722	131.3	1.1400
117.5	1.1718	131.8	1.1396
118.5	1.1706	134.4	1.1382
119.6	1.1692	135.8	1.1372
120.0	1.1688	137.6	1.1364
120.8	1.1678	140.2	1.1349
121.6	1.1668	143.2	1.1328
121.8	1.1666	144.4	1.1319
122.1	1.1662	147.3	1.1299
122.3	1.1660	148.1	1.1293
122.8	1.1462	150.5	1.1277
123.6	1.1454	152.5	1.1263
123.7	1.1453	155.5	1.1242
124.4	1.1446	158.7	1.1219
124.5	1.1445	161.4	1.1201
126.3	1.1434	164.2	1.1181
126.5	1.1433	165.6	1.1171
127.6	1.1426	167.8	1.1155
128.5	1.1420		

CHAPTER VI

EXPERIMENTAL STUDIES ON THE OPTICAL REFLECTIVITY OF THE FREE SURFACE OF NEMATOGENS IN THE ISOTROPIC PHASE

Introduction

According to the theory outlined in chapter **II**, an excess orientational order is expected to develop at the free surface of the smectic, nematic and even the isotropic phases. The excess surface order should manifest itself as a positive slope in the γ - T characteristic, and this is indeed confirmed by our experiments on a number of compounds (as described in chapters **IV** and **V**). Recently Nielsen et al¹ have detected by Xray methods a smectic order at the free surface of **8 OCB** in the nematic **and** isotropic phases. Here we describe an **experiment** on optical **reflecti-**

vity of the free surface of a nematogen in the isotropic phase which provides a direct evidence of the existence of a surface orientational order.

Principle of the method

We shall first outline the principle underlying the method. We shall consider a very simple model consisting of a layer of homeotropically aligned molecules of thickness τ on the isotropic bulk liquid as shown in fig.6.1. As the molecules of both the compounds studied here, 4'-n-Pentyl-4-cyanobiphenyl (5CB) and 4'-n-heptyl-4-cyanobiphenyl (7CB), have strong polar end groups, they are likely to align homeotropically at the free surface as predicted by Parsons.² Thus the simplified model does bear some similarity to the actual situation.

For such a model, the optical reflectivity (defined as the ratio of the reflected to the

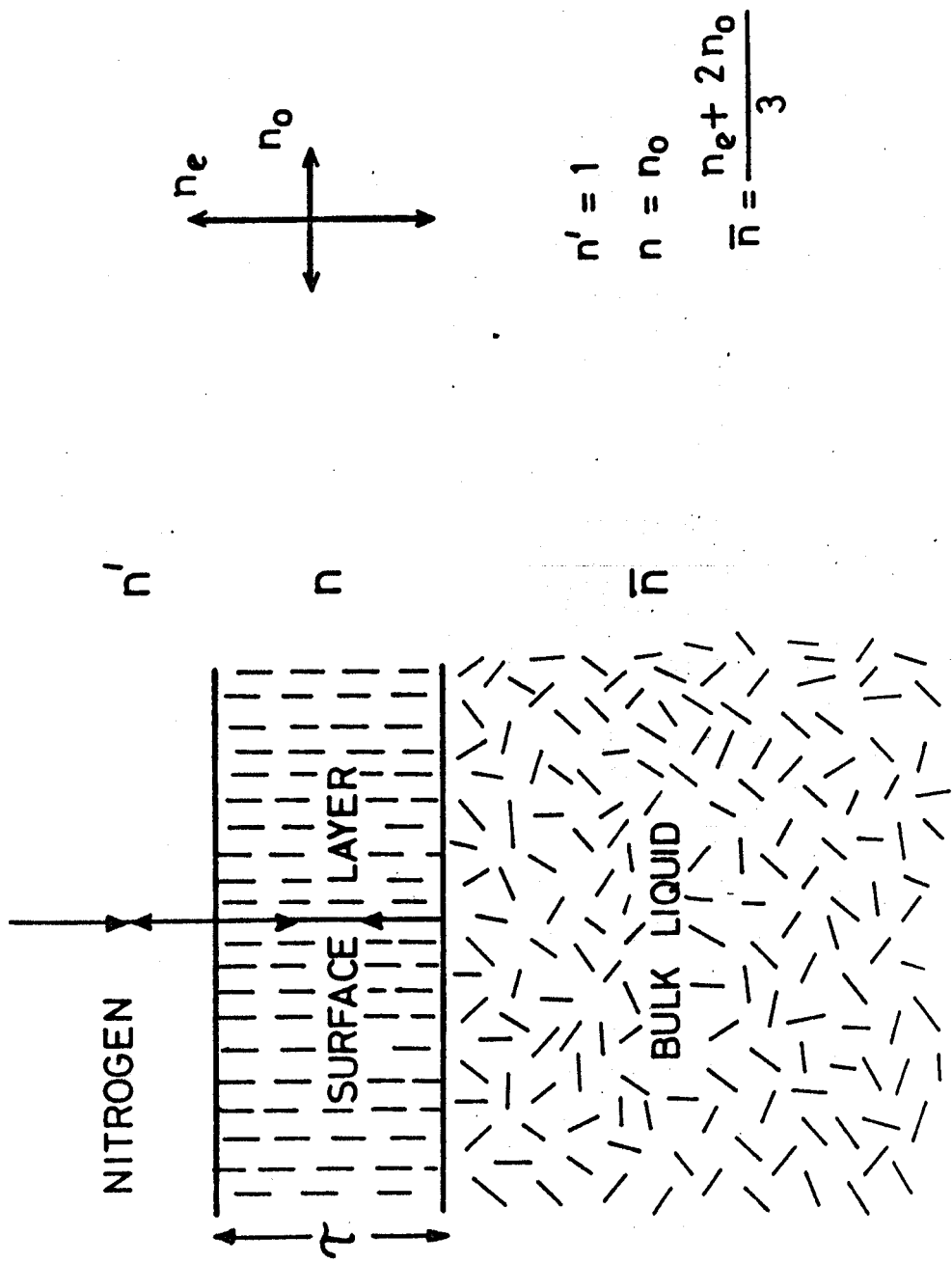


Fig.6.1: A simple model of the surface order in the isotropic phase.

incident intensities) is given by

$$R_o = \left(\frac{n_o - n'}{n_o + n'} \right)^2 \left(\frac{1 + a^2 - 2a \cos \delta}{1 + b^2 - 2b \cos \delta} \right) \quad (1)$$

where

$$a = \left(\frac{n_o + n'}{n_o - n'} \right) \left(\frac{n_o - \bar{n}}{n_o + \bar{n}} \right) \quad (2)$$

and

$$b = \left(\frac{n_o - n'}{n_o + n'} \right) \left(\frac{n_o - \bar{n}}{n_o + \bar{n}} \right) \quad (3)$$

Here n_o is the ordinary index of the ordered layer, $\bar{n}$ is the refractive index of the isotropic liquid ($\bar{n} = \frac{n_e + 2n_o}{3}$ where n_e is the extraordinary index of refraction of the ordered layer) and n' that of air (nitrogen). δ is the phase difference between the reflections from the top and bottom surfaces of the ordered layer. τ and δ are related as

$$\tau = \delta \lambda / 4\pi n_o \quad (4)$$

Using (1) and (4), R_0 can be calculated for a given thickness τ . We find that R_0 is maximum for $\tau = 0$ and decreases as τ increases. We have calculated R_0 for various values of τ using $n_o = 1.528$ and $n_e = 1.719$ in the case of 5CB, and $n_o = 1.516$ and $n_e = 1.701$ in the case of 7CB. The n values are due to Karat and Madhusudana.³ The curves obtained for a range of $\tau = 0$ to 350 Å are given in figures 6.2 and 6.3.

In this model, we have assumed the interface between the liquid crystal and vapour to be sharp, whereas in reality the density varies gradually across the interface (fig. 2.1). The refractive index n_o is considered to be constant over the layer thickness τ , but actually it varies with the depth, since the orientational order parameter slowly assumes the bulk value over the correlation length. Hence we can say that the model is oversimplified. Nevertheless

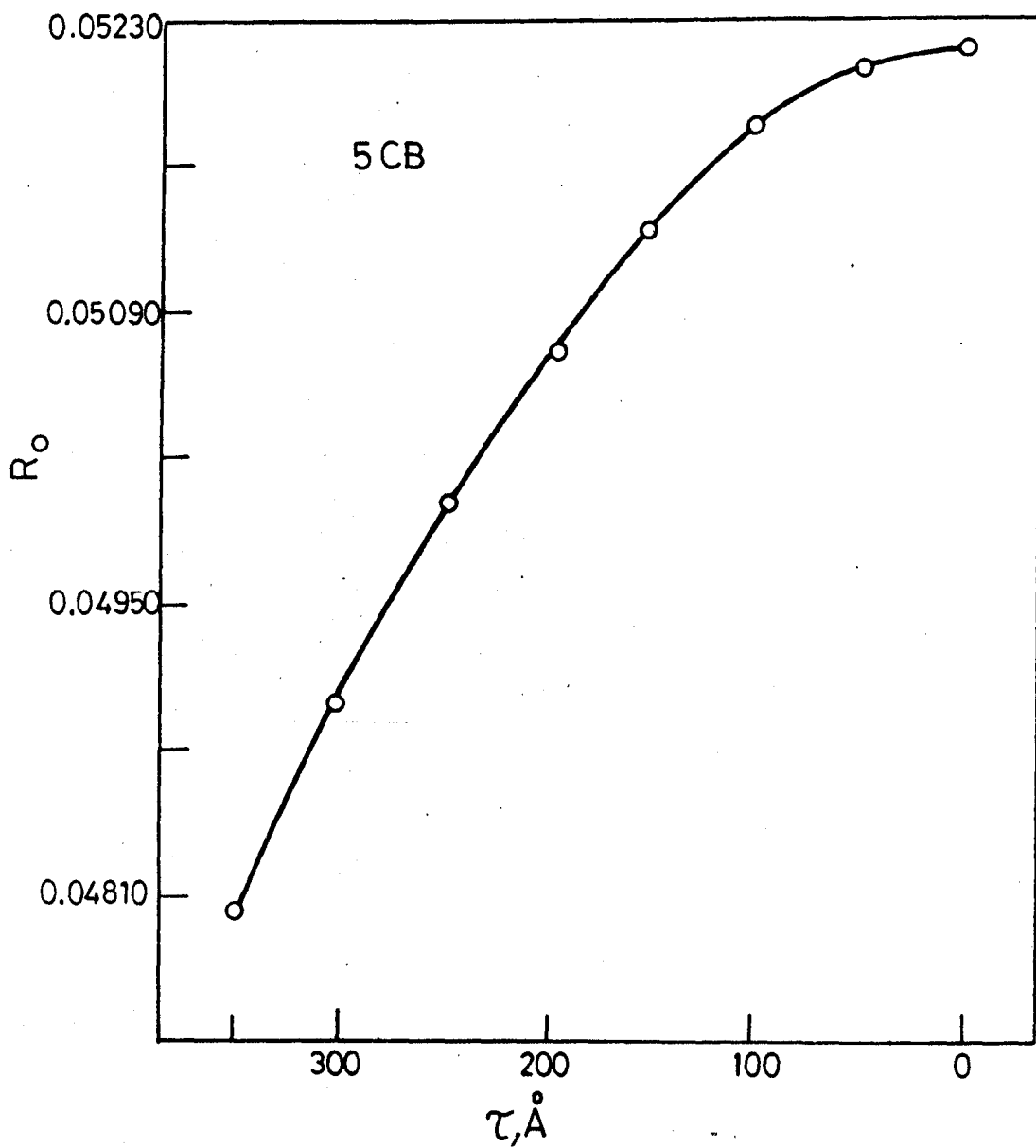


Fig. 6.2: Theoretical $R_o - \tau$ curve for 5CB obtained from the model.

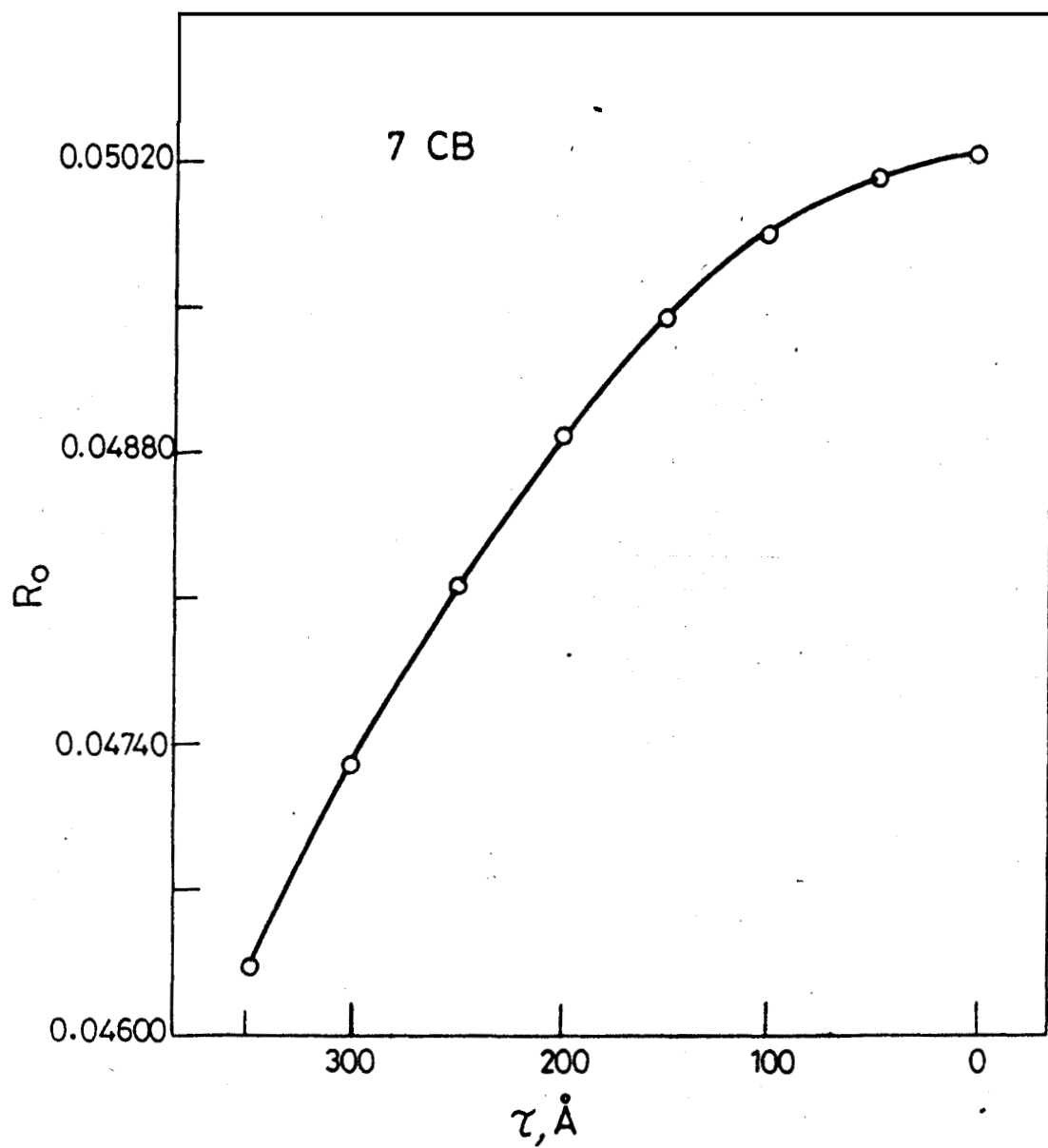


Fig.6.3: Theoretical R_0 - τ curve for 7CB obtained from the model.

it suggests qualitatively that there should be a decrease in reflectivity with an increase in the layer thickness.

Experimental set up

The experimental set up is as shown in fig. 6.4. The sample was taken in a wide cylindrical glass vessel (v), The bottom of the glass vessel was made inclined so that the reflections from the bottom surface were deviated well away from the vertical direction. It was rigidly fixed in a heavy copper block (c_2), and the copper block itself was rigidly fixed in a massive air-tight copper chamber (c_1). The chamber was electrically heated and could be maintained at any desired constant temperature. The temperature was measured using a copper constantan thermocouple which was calibrated earlier using a standard thermometer. The accuracy of the measurement was $\pm 0.02^\circ\text{C}$. The junction of the thermocouple

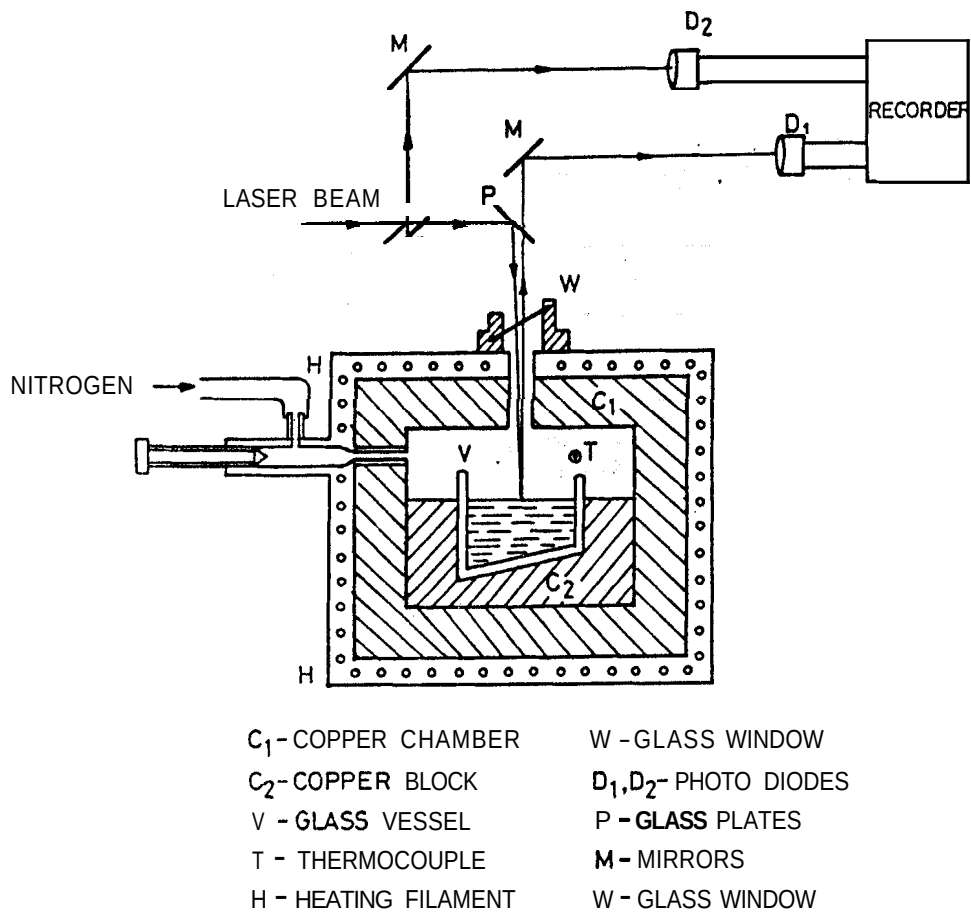


Fig. 6.4: Schematic diagram showing the experimental set up for the optical reflectivity studies.

was placed very close to the surface of the liquid crystal. Pure and dry nitrogen was flushed through the chamber for nearly 30 minutes and then the nozzles were closed so that the nitrogen was trapped inside the chamber. A beam of light from a helium-neon laser (Spectraphysics 125A) was directed at nearly normal incidence (angle of incidence $< 0.5^\circ$) on to the surface of the **sample** through the **optically** flat glass window provided at the top of the chamber. The window was also made inclined to the normal to avoid the reflections from **it** entering the optical diode used for measuring **the** intensity of the reflected beam.

The reflected beam from the surface of the liquid crystal was directed ~~onto~~ a photodiode (MRD500). The output of the photodiode (R_1) was fed to one of the channels of a multichannel strip chart recorder. It was ascertained that reflections other than that from the surface of the liquid crystal did not enter

the optical diode. **This** was checked **by** ensuring that the output of the diode was zero when the vessel was empty.

In order to allow for any fluctuations **in** the intensity of the laser beam, **a part** of the incident beam reflected from a glass plate was directed onto a similar diode **and** the output (R_2) of **this** diode was fed to another channel of the recorder. The two channels were calibrated earlier using a standard voltage source. R_1 and R_2 were **simultaneously** recorded at a number of steady temperatures in the isotropic **phase**. The ratio $R = R_1/R_2$ at each temperature is proportional to the reflectivity at that temperature. A curve **was** plotted with the value of R vs. the temperature (T).

Results and discussions

Both the compounds studied here were synthesized in our laboratory. Both are nematic liquid

crystals at room temperature. The **N-I** transition temperature of 5CB was **34.7°C** and that of 7CB was **42.3°C**. The structural formula of 5CB is given in **fig.4.5** (chapter IV). 7CB is the seventh homologue of the same series.

The **R-T** curves obtained for these compounds are given in figures 6.5 and 6.6. In both the cases we find ~~that~~ **R** increases with **T** and attains a **maximum** value at about **1°C** above **T_{NI}**. On further increase of temperature the value of **R** starts decreasing slightly probably due to the thermal fluctuations of the surface and decrease in the refractive index with temperature.

A qualitative comparison between the experimental **R-T** curves and the theoretical **R₀ - τ** curves indicates that there is an ordered layer at the free surface, and the variation in the thickness of this ordered layer is really responsible for the experi-

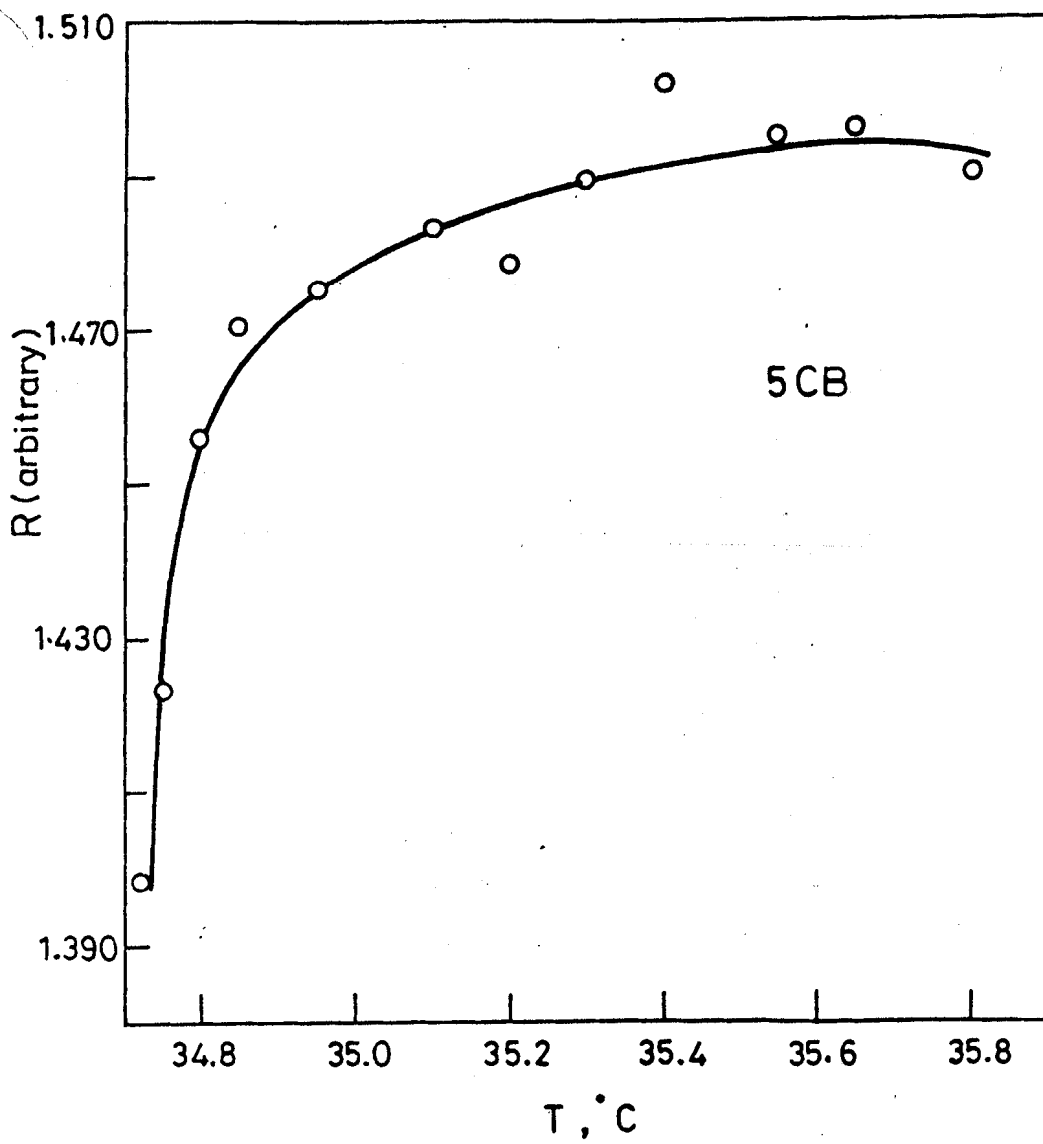


Fig.6.5: Variation of R with T for 5CB (experimental)

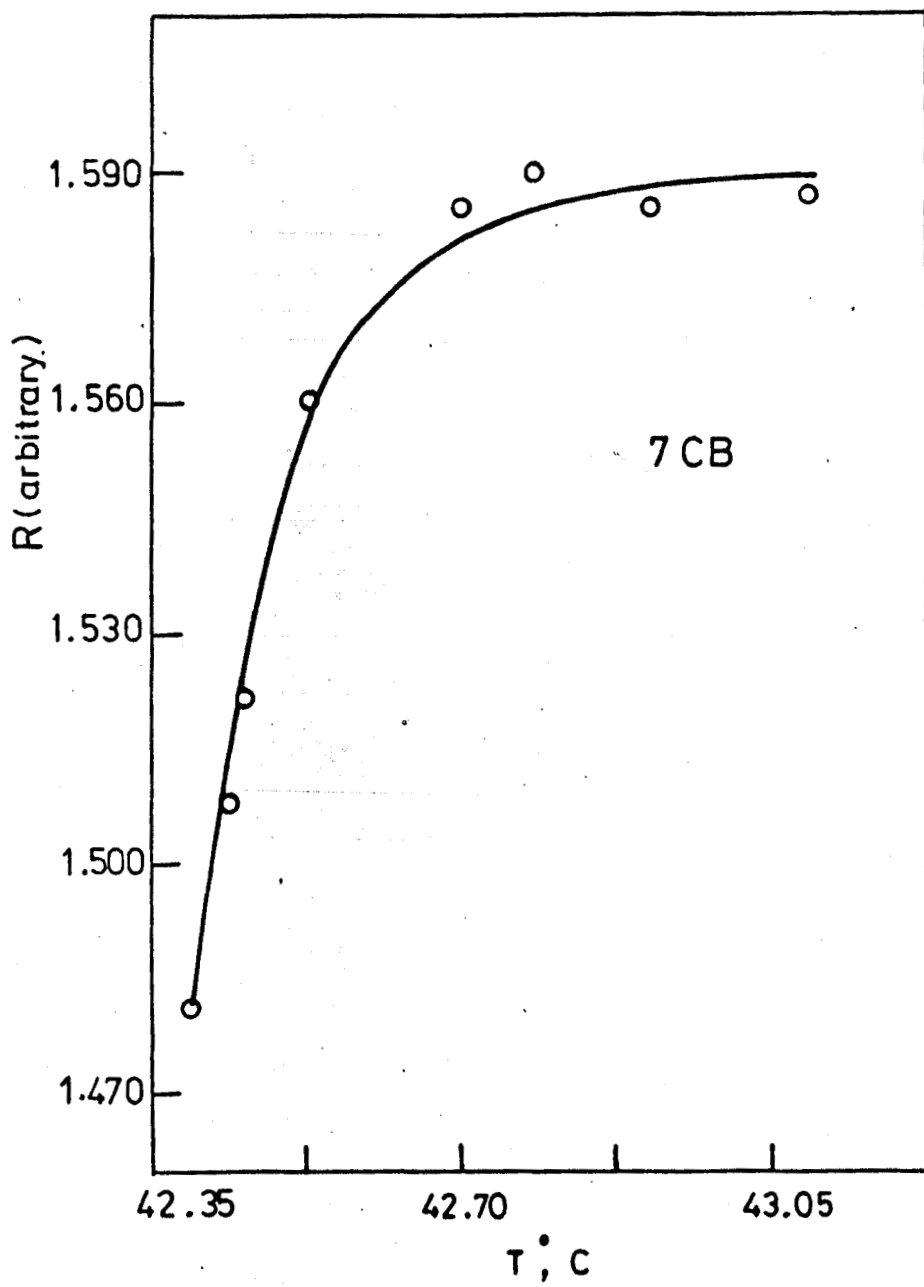


Fig. 6.6: variation of R with T for 7CB (experimental)

mentally observed variation of R . We can conclude from the curves that the layer thickness at the free surface builds up in the isotropic phase as one approaches the N-I transition temperature.

As explained earlier, the model is an oversimplified one and hence quantitative comparison between the experimental and theoretical curves are not significant. The present study is just a preliminary one. We hope to improve the experimental technique as also develop a more realistic model before attempting to interpret the results and draw quantitative conclusions.

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