

CHAPTER VI

DIELECTRIC DISPERSION STUDIES IN RE-ENTRANT NEMATOGENS

6.1 Introduction

It is well known that the dielectric constants of liquid crystals are frequency dependent. Because of the orientational order in the medium, $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ have different frequency dependences. $\epsilon_{\perp}$ exhibits only the normal Debye relaxation which usually occurs in the GHz region. But $\epsilon_{\parallel}$ shows an additional dispersion in the MHz region or even in the KHz region. The low frequency relaxation was first observed by Maier and Meier¹ in alkoxyazoxybenzenes. They showed that in the radio frequency region $\epsilon_{\parallel}$ exhibits a dispersion while $\epsilon_{\perp}$ remains constant in this region.

The low frequency relaxation of $\epsilon_{\parallel}$ is due to the hindrance to the reorientation of the dipole. The dipole moment μ of a molecule making an angle θ

with the long molecular axis can be resolved into two components. The longitudinal component in the direction of the long molecular axis is $\mu_{\parallel} = \mu \cos \theta$ and the transverse component $\mu_{\perp} = \mu \sin \theta$. The reorientation of $\mu_{\parallel}$ is hindered due to the molecular order. This results in a low frequency dispersion of $\epsilon_{\parallel}$. The transverse component $\mu_{\perp}$ can reorient freely by rotation around the long axis and $\epsilon_{\perp}$ exhibits a dispersion in the microwave region. Because of imperfect order, $\mu_{\perp}$ also contributes to $\epsilon_{\parallel}$ leading to a second dispersion of $\epsilon_{\parallel}$ in the microwave region. In the isotropic phase, the dielectric constant exhibits the usual Debye type relaxation.

Meier and Saupe² extended the Debye theory³ of dielectric relaxation in liquids to nematics. Martin et al.⁴ refined the theory. It was shown by them that the relaxation time τ_R corresponding to the reorientation of $\mu_{\parallel}$ is orders of magnitude higher than the normal Debye relaxation time τ_0 in the isotropic

phase. The ratio τ_R/τ_0 is called the retardation factor g . The value of g was calculated as a function of the orientational nematic potential q . The relationship between g and q was given by the expression

$$g = [kT/q] [\exp(q/kT) - 1]$$

or $g \approx [kT/q] \exp[q/kT].$

In the isotropic phase, the resistance to the reorientation of the dipole moment is mainly due to the viscosity (η) of the medium. The temperature dependence of this can be expressed as

$$\eta \propto \exp[q_\eta/kT]$$

where q_η is the activation energy due to viscosity effects. Now, the relaxation time τ_0 in the isotropic phase is $\propto \eta/kT$.

From the definition of the retardation factor, the relaxation time $\tau_R = \tau_0 g$, and hence

$$\tau_R \propto \exp[(q + q_\eta)/kT]$$

or $\tau_R \propto \exp[w/kT]$

where $w = [q + q_\eta]$ is the total activation energy for dielectric relaxation.

The relaxation time $\tau_R = \frac{1}{2\pi f_R}$ where f_R is the frequency of relaxation. Hence $f_R \propto \exp[-w/kT]$.

A plot of $\log f_R$ versus $1/T$ should be a straight line, the slope of which gives the activation energy w . Thus, the total activation energy can be calculated by measuring the temperature variation of f_R of $\epsilon_{||}$.

The dielectric constant $\epsilon_{||}$ is actually a complex quantity. $\epsilon_{||} = \epsilon'_{||} + i \epsilon''_{||}$ where the real part ($\epsilon'_{||}$) describes the ordinary dielectric constant and the imaginary part ($\epsilon''_{||}$) the dielectric losses associated with the relaxation process. A Cole-Cole diagram of $\epsilon''_{||}$ versus $\epsilon'_{||}$ indicates the nature of relaxation.

The radio frequency dispersion of $\epsilon_{||}$ has been extensively studied for a number of strongly polar compounds by Ratna and Shashidhar.^{5,6}

We have measured the low frequency relaxation of $\epsilon_{||}$ in the normal nematic, smectic A and the re-entrant

nematic phases of both the pure compounds, 11 CPMBB and 12 CPMBB and of the binary mixture 6 OCB/8 OCB.

6.2 Experimental

The experimental details regarding We cell used for measurements, the heater and the temperature control are described in chapter V. The sample, sandwiched between two tin oxide coated plates was cooled in the presence of a magnetic field as mentioned in section 3 of chapter V, for better alignment. The temperature could be measured to within $\pm 0.025^{\circ}\text{C}$, while the constancy of temperature during each determination of the frequency of relaxation was $\pm 0.1^{\circ}\text{C}$.

The dielectric dispersion was measured in the frequency region 1 KHz to 10 MHz. The dispersion of ϵ'' in the frequency range 1 KHz to 20 KHz was measured by the Wayne Kerr bridge (B642) using an external source and detector. For measurements in the frequency range 100 KHz to 10 MHz another Wayne Kerr bridge (B602) was

used in conjunction with a Wayne Kerr SR268L source and detector. The maximum error in the determination of the frequency of relaxation (f_R) of $E_{||}$ is estimated to be 7%.

The dielectric loss ($\epsilon''_{||}$) and the dielectric constant ($\epsilon'_{||}$) were both determined. The measured reactance was corrected for the series inductance also. As expected, $\epsilon'_{||}$ showed a dispersion in the frequency range covered, while $\epsilon'_{\perp}$ remained constant. However, the loss $\epsilon''_{\perp}$ was not zero due to non-zero ionic conductivity. This value of $\epsilon''_{\perp}$ was used to correct $\epsilon''_{||}$ as suggested by Rondlez and Mircea-Roussel.⁷

6.3 Results and discussion

A representative curve showing the variation of the loss $\epsilon''_{||}$ with frequency is shown in figure 6.1 for all the three systems studied. The maximum of this curve gives the frequency of relaxation (f_R).

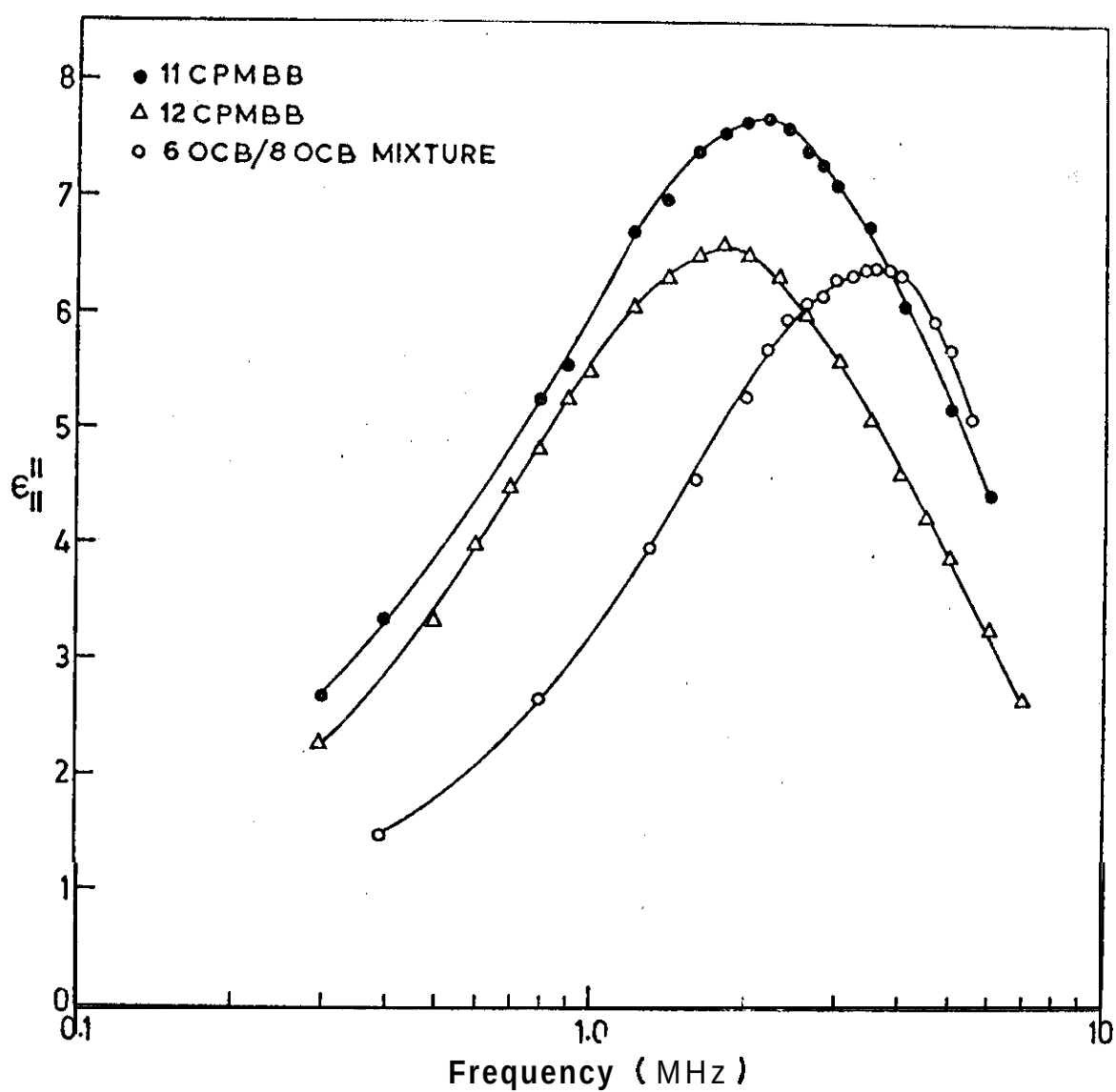


FIGURE 6.1

Dielectric loss ($\epsilon''_{||}$) as a function of frequency for 11 CPMBB (at 123.925°C), 12 CPMBB (at 121.025°C) and 6 OCB/8 OCB mixture (at 49.925°C).

The plot of ϵ''_{11} versus ϵ'_{11} was a semicircle with the centre lying on the $\epsilon''_{11} = 0$ axis denoting a single relaxation time.⁸ For both the pure compounds and the mixture studied, the typical Cole-Cole plots at a certain temperature are shown in figures 6.2(a), 6.2(b) and 6.2(c). The plot of ϵ''_{11} versus frequency along with the Cole-Cole plot is enough to describe the relaxation process completely.

The plots of $\log f_R$ versus $1/T$ for the, pure compounds and the mixture are given in figures 6.3 to 6.5. It is seen that for both the pure compounds (figures 6.3 and 6.4), f_R in the re-entrant nematic phase is very low, under 10 KHz region. But for the mixture (figure 6.5), f_R occurs in the 100 KHz region. For 12 CPMBB, we could determine f_R at only two temperatures in the re-entrant nematic phase since it is a highly metastable phase with a relatively short range. The activation energies evaluated from the $\log f_R$ versus $1/T$ plots are given in table 6.1. It is seen from the table that the value of

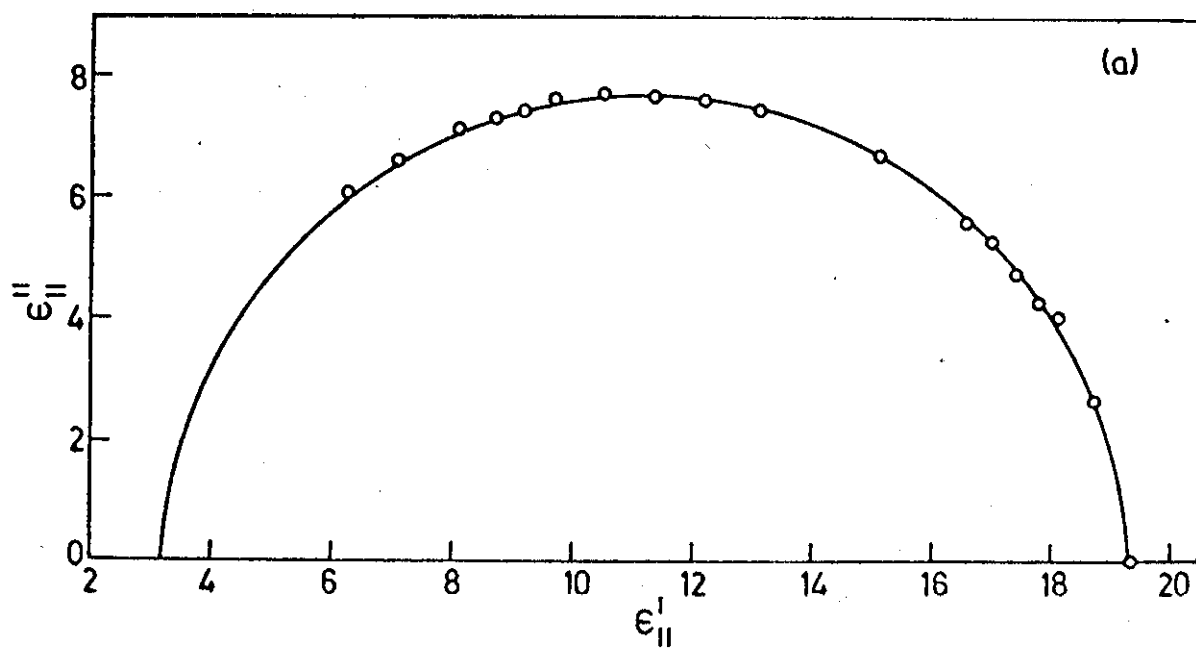


FIGURE 6.2a

Cole-Cole plot for 11 CPMBB at 123.925°C

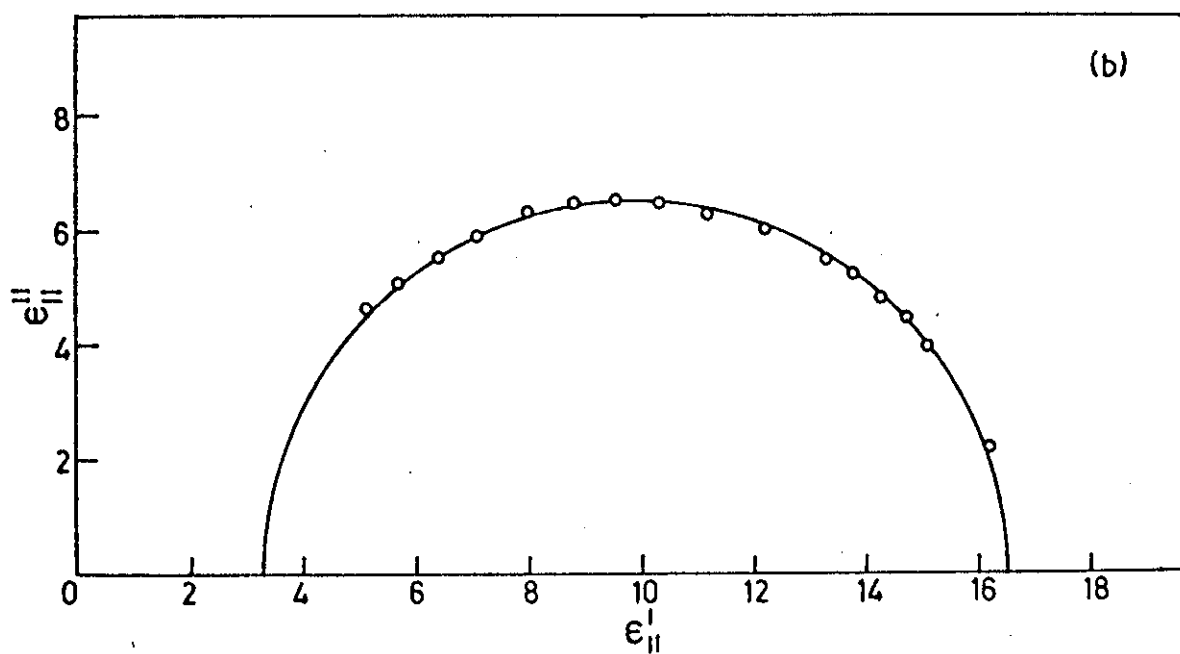


FIGURE 6.2b

Cole-Cole plot for 12 CPMBB at 121.025°C

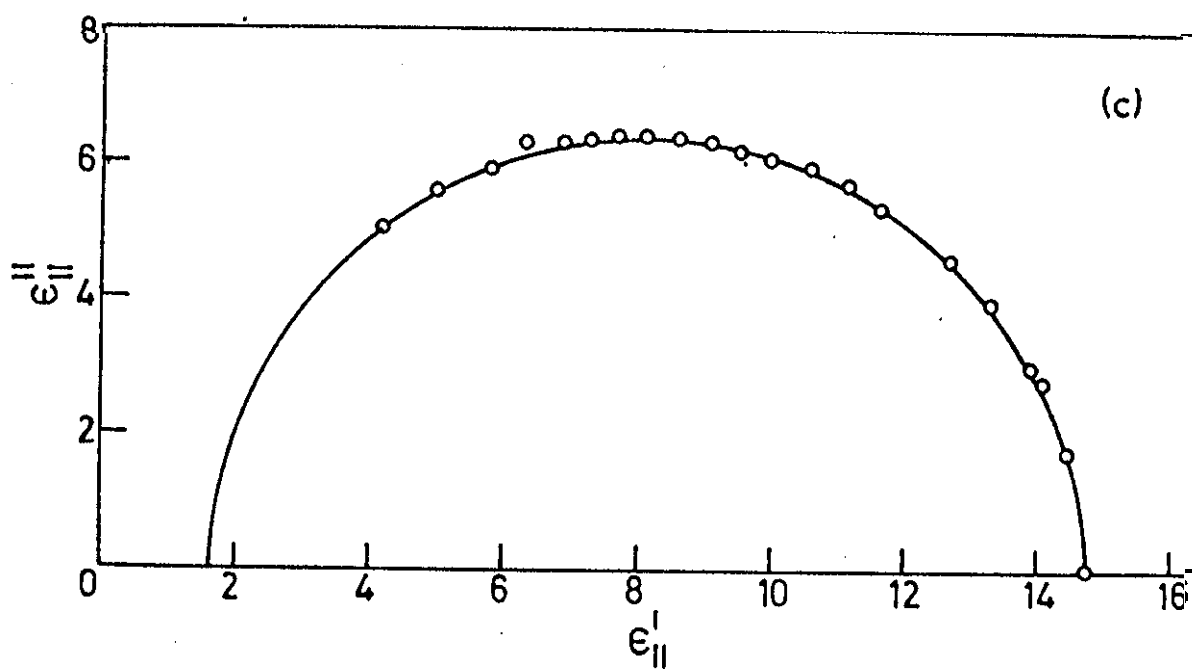


FIGURE 6.2c

Cole-Cole plot for 6 OCB/8 OCB mixture at
49.925°C

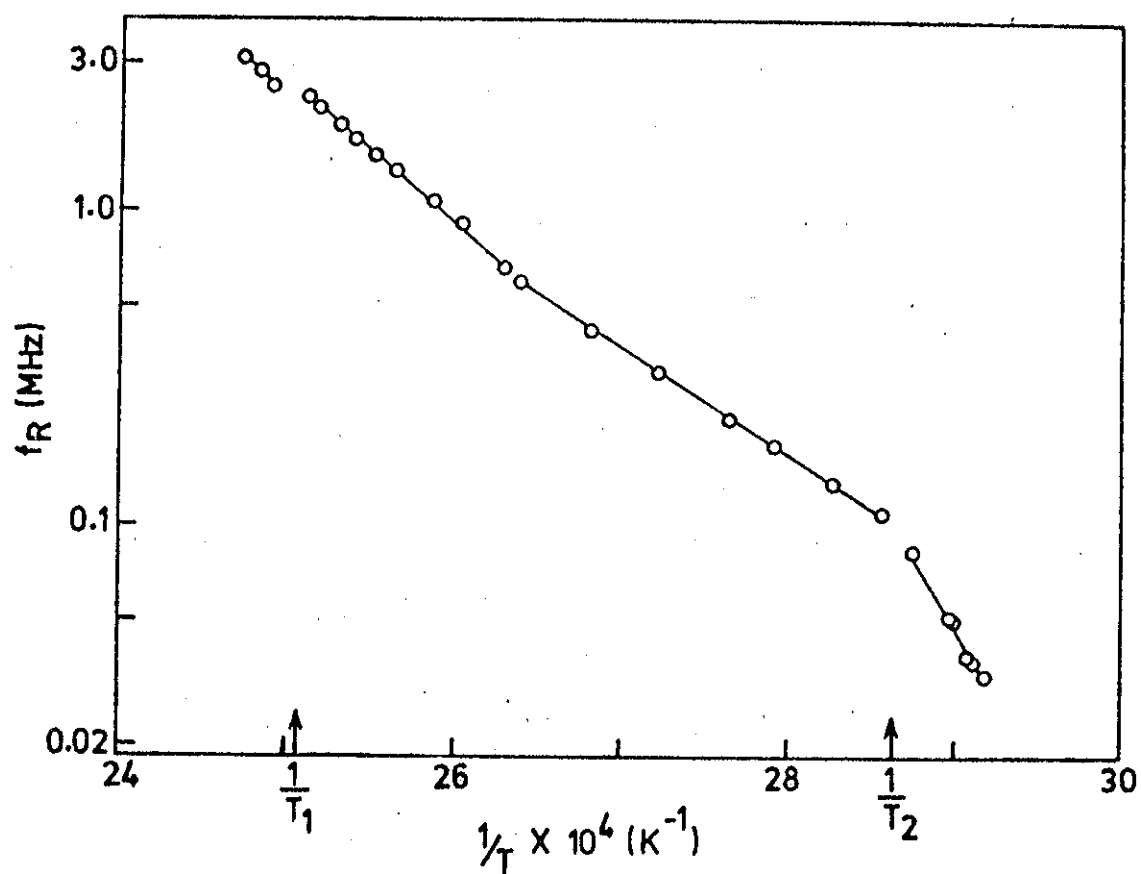


FIGURE 6.3

Logarithmic plot of frequency of relaxation (f_R) versus $1/T$ for 11 CPMBB.

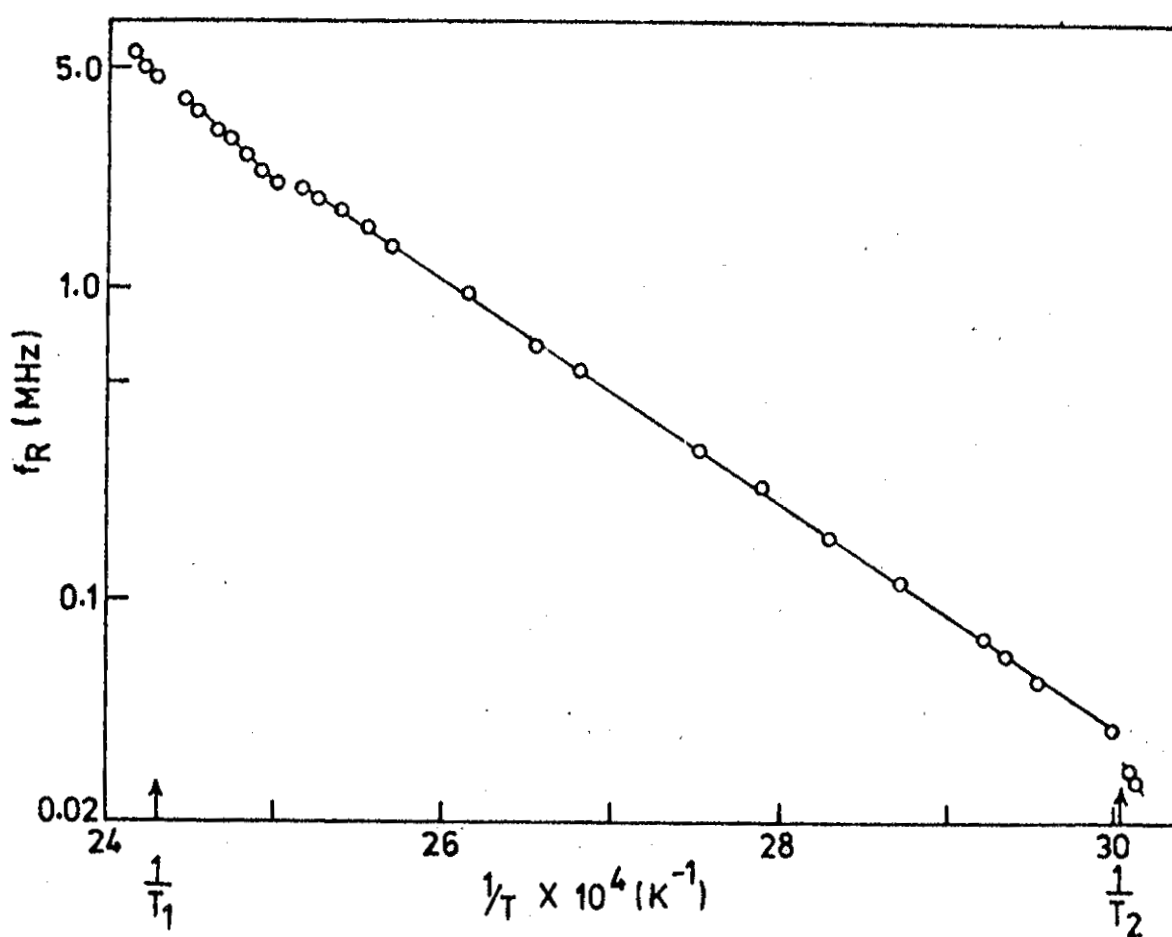


FIGURE 6.4: Logarithmic plot of frequency of relaxation (f_R) versus $1/T$ for 12 CPMBB

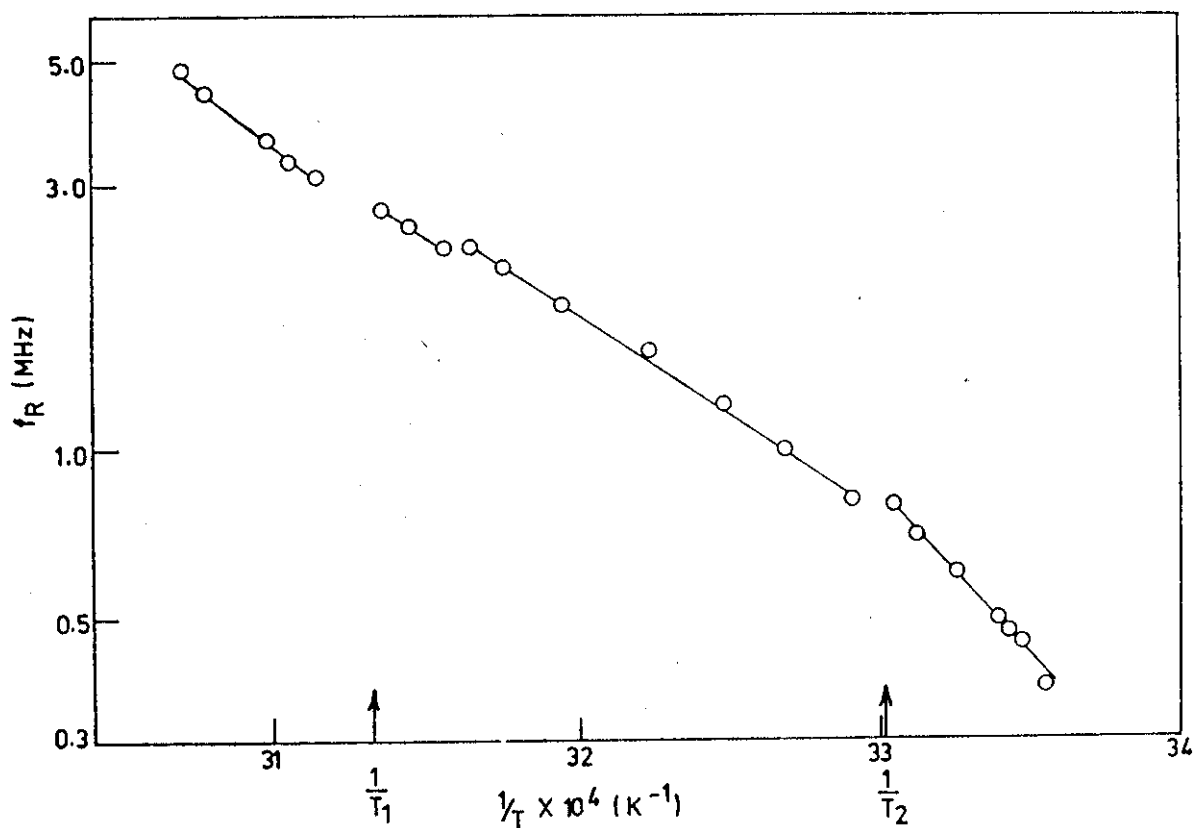


FIGURE 6.5: Logarithmic plot of frequency of relaxation (f_R) versus $1/T$ for 6 OCB/8 OCB mixture.

Table 6.1

Activation energy (w in eV) for 11 CPMBB, 12 CPMBB
and 6 OCB/8 OCB mixture

Activation energy	Compound		
	11 CPMBB	12 CPMBB	6 OCB/8 OCB mixture
w_{nematic}	1.02	1.14	0.82
$w_{1 \text{ smectic}}$	0.92	0.97	0.73
$w_{2 \text{ smectic}}$	0.66	0.70	0.71
$w_{\text{reentrant nematic}}$	1.82	1.79	1.71

the activation energies for the corresponding mesophase of 91 CPMBB and 12 CPMBB are about the same. The mixture has lower activation energies.

Several other interesting features which are common to all the three systems are observed. They are -

(I) The normal nematic phase has a higher activation

energy than the smectic phase. A similar observation has been made by Druon and Wacrenier⁹ on 8 OB. This is in contrast to what one would expect since the smectic phase is more ordered and has higher viscosity than the nematic. It appears that the bilayer structure of the smectic A phase somehow makes the reorientation of the molecules easier.

(11) In the smectic phase, the plot consists of two distinct straight lines, with different slopes (or different w) indicative of some sort of structural change in the system. It is interesting to note that the temperature at which this change in slope occurs in the smectic phase roughly corresponds to the temperature at which ΔC_p shows a reversal in the trend discussed in section 3B of chapter V. It should however be mentioned here that the differential scanning calorimetry (DSC) runs taken for these compounds with the maximum possible sensitivity (0.1 mcal/sec) failed to show any transition at these temperatures. Also, no textural changes could be

observed. When viewed under a polarising microscope a fan shaped texture persisted throughout the smectic phase.

The difference between the activation energies w_1 (smectic) and w_2 (smectic) is more pronounced in the pure compounds than in the mixture (see table 6.1).

The activation energy w_2 in the lower temperature range of the smectic phase is less than w_1 in the higher temperature range of the same phase. It is also significantly less than the activation energy in the re-entrant nematic phase. This would seem to indicate that as far as the dielectric relaxation mechanism is concerned, the behaviour in the lower temperature range of the smectic phase may not be a pretransition effect. However, as we shall see in the next chapter, the transport properties (in particular the electrical conductivity) do show a marked pretransitional effect prior to the smectic A - re-entrant nematic transition point.

(iii) The most important observation is made that

the re-entrant nematic phase has a much higher activation energy than the normal nematic phase, showing that the hindrance to the reorientation is more in the re-entrant nematic phase. This is the first experimental evidence of the molecular associations being different in the two nematic phases, showing therefore the sensitivity of the experimental technique to detect this difference in the two phases on a molecular level. It should be mentioned here that neither the orientational order determination¹⁰ nor the elastic constant determination¹¹ could defeat this difference.

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CHAPTER VII

ELECTRICAL CONDUCTIVITY MEASUREMENTS ON RE-ENTRANT NEMATOGENS

7.1 Introduction

It was first; shown by Svedberg¹ as early as 1914 that for a nematic, the electrical conductivity measured along the optic axis ($\sigma_{||}$) is greater than that measured normal to it ($\sigma_{\perp}$). No conductivity measurements were carried out on smectics however, for a long time. Carr,² on the basis of the effect of electric field studies on ethyl-p-[(p'-methoxybenzylidene)-amino]cinnamate (EMC), suggested that in We smectic A phase, the conductivity measured normal to the long molecular axis ($\sigma_{\perp}$) should be greater than the conductivity parallel to the axis ($\sigma_{||}$). This was indirectly confirmed by Rondelez³ who measured the temperature dependence of $\sigma_{||}$ and $\sigma_{\perp}$ in the nematic phase of 4,4'-di-heptyloxyazoxybenzene (HOAB) which exhibits a smectic C phase at lower temperatures. He found that the ratio of the electrical conductivities

$R = \sigma_{||}/\sigma_{\perp}$, decreases with decrease of temperature from the nematic-isotropic transition point (T_{NI}) over the entire nematic range. The value of R which is equal to 1 at T_{NI} falls to about 0.7 at the nematic-smectic C transition. He attributed this to the existence of the smectic like short range order or cybotactic groups⁴ in the nematic phase. Subsequently, Mircea-Roussel and Rondelez⁵ and also Heppke and Schneider⁶ observed a similar behaviour of R in the nematic phase of all the higher homologues of the 4,4'-di-alkoxyazoxy series.

The first detailed experimental studies of electrical conductivity in the smectic A phase was by Mircea-Roussel et al.⁷ who measured $\sigma_{||}$ and $\sigma_{\perp}$ in the smectic and nematic phases of a number of compounds. The compounds studied by them are the following: compounds belonging to the alkoxybenzylidene alkyylaniline series (nO.m series), p,p'-di-heptylazoxybenzene (HAB), N-p-cyanobenzylidene-p-n-octyloxyaniline (CBOOA), 4'-n-octyl-4-cyanobiphenyl (8CB) and 4'-n-octyloxy-4-cyanobiphenyl (8 OCB).

All the compounds show pretransitional effects in the nematic phase near the nematic-smectic A transition temperature. But with regard to the electrical conductivity studies in the smectic A phase, the compounds fall into two distinct groups. The first group consists of the compounds of the nO.m series. The compound HAB also follows the same characteristics of the nO.m series as regards the conductivity. The second group consists of the cyano compounds CBOOA, 8CB and 8 OCB.

For the compounds of the first group, $\sigma_{\parallel}$ decreases continuously with decreasing temperature in the nematic and smectic phases and then saturates in the lower temperature range of the smectic phase. But the behaviour of $\sigma_{\perp}$ is more surprising. With decrease of temperature, $\sigma_{\perp}$ decreases in the nematic phase and then begins to increase near the nematic-smectic A transition point. This increase of $\sigma_{\perp}$ is considerable so much so that $\sigma_{\perp}$ becomes greater than $\sigma_{\parallel}$. In the lower temperature range of the smectic A phase, $\sigma_{\perp}$ becomes at least five

times greater than $\sigma_{\parallel}$. Thus the compounds are characterised by strong conductivity anisotropy and a very low value of R in the smectic A phase.

For the compounds of the second group, $\sigma_{\parallel}$ differs only slightly from $\sigma_{\perp}$ and the variation of the conductivities with temperature is different from that observed for the compounds of the first group. Here, both $a_{\parallel}$ and $a_{\perp}$ decrease continuously with temperature. The ratio R , after an initial rise near the nematic-isotropic transition point, decreases slowly with fall in temperature. The rate of decrease is very slow in the smectic A phase. In 8 OCB, R attains the value 1 in the smectic A phase and hence there is no conductivity anisotropy. 8CB has also a behaviour similar to 8 OCB. In CBOOA, R decreases to a value slightly less than 1 (it is actually 0.85) in the smectic A phase. Hence the strong anisotropy in conductivity observed in the compounds of the first group in the smectic A phase is not found here.

It is interesting to note that all the compounds

of the second group are strongly polar, which are known to possess a bilayer arrangement in the smectic A phase,⁸ while the compounds belonging to the first group have a layer spacing approximately equal to the molecular length. Hence the different behaviour in the transport properties was attributed to the difference in structure between the two groups of compounds.

We saw in chapter V that the mean dielectric constant $\bar{\epsilon}$ exhibits a surprising variation with temperature. It decreases first with decrease in temperature from the nematic-isotropic transition point and the minimum value is reached in the smectic range. On further cooling, it increases as the re-entrant nematic phase was approached. This was attributed to some structural change in the system. It can be inferred that the antiparallel order, which was increasing till the maximum value is reached in the smectic phase (when $\bar{\epsilon}$ is minimum) decreases as the mean dielectric constant increases near the re-entrant nematic phase. In chapter VI it was observed that

the molecular associations are significantly different in the normal nematic and re-entrant nematic phases. The plot of $\log f_R$ versus $1/T$ gave two straight lines with different slopes indicating different activation energies. This means that the re-entrant phenomenon is associated with some kind of change in the system at the molecular level. To find out whether such structural changes have any effect on the transport properties, we have studied the temperature variation of the principal electrical conductivities of two re-entrant nematogens.

7.2 Experimental

The compounds studied are 12 CPMBB and 35.8% weight mixture of 6 OCB in 8 OCB (see table 5.1 for transition temperatures).

The conductivities $\sigma_{||}$ and $\sigma_{\perp}$, were determined at 1592 Hz using a Wayne Kerr (B642) autobalance bridge using the experimental set up described in section 3A of chapter V. As mentioned in that section, the sample

sandwiched between two tin oxide coated plates was aligned by a strong magnetic field (15 KGauss). The well aligned smectic A was obtained by cooling an aligned nematic in the presence of the magnetic field.

The accuracy of the relative variation of $a_{||}$ and $a_{\perp}$ was $\pm 0.2\%$ while the absolute accuracy is estimated to be 3 to 4%.

7.3 Results and Discussion

The variation of $a_{||}$, $a_{\perp}$ and R in $(a_{||}/a_{\perp})$ with temperature for 12 CPMBB and 6 OCB/8 OCB mixture are shown in figures 7.1 and 7.2 respectively.

In both the systems studied, R shows an interesting variation with temperature. We shall discuss the nature of variation of $a_{||}$, $a_{\perp}$ and R with temperature for the pure compound and the mixture separately.

a) 12 CPMBB

In the vicinity of the nematic-isotropic transition point (T_{NI}) $a_{||}$ slightly increases with decrease in tempe-

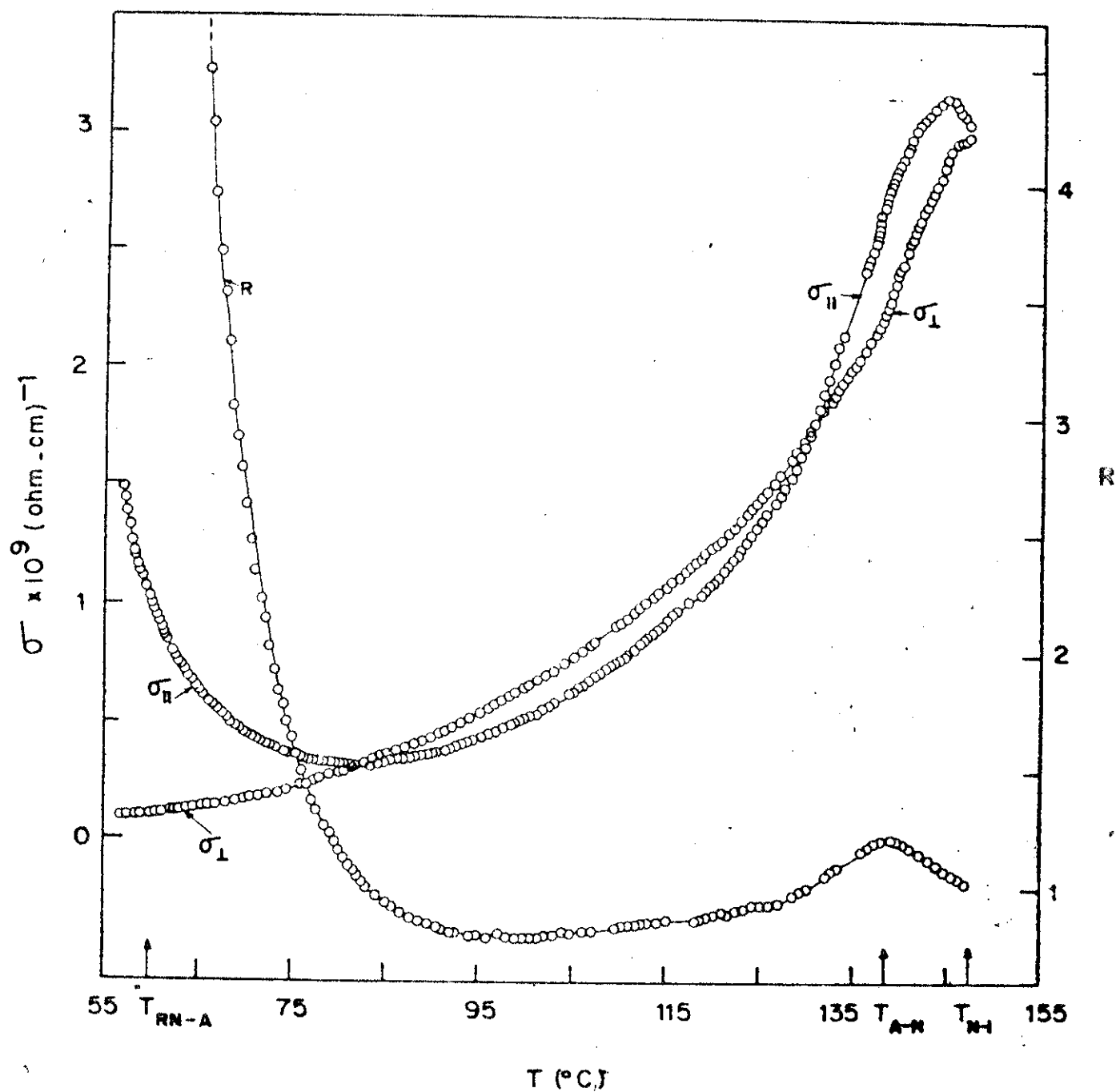


FIGURE 7.1

The principal electrical conductivities $\sigma_{\parallel}$ and $\sigma_{\perp}$ and their ratio $R = \sigma_{\parallel}/\sigma_{\perp}$ of 12 CPMBB as functions of temperature in the nematic, smectic A and re-entrant nematic phases.

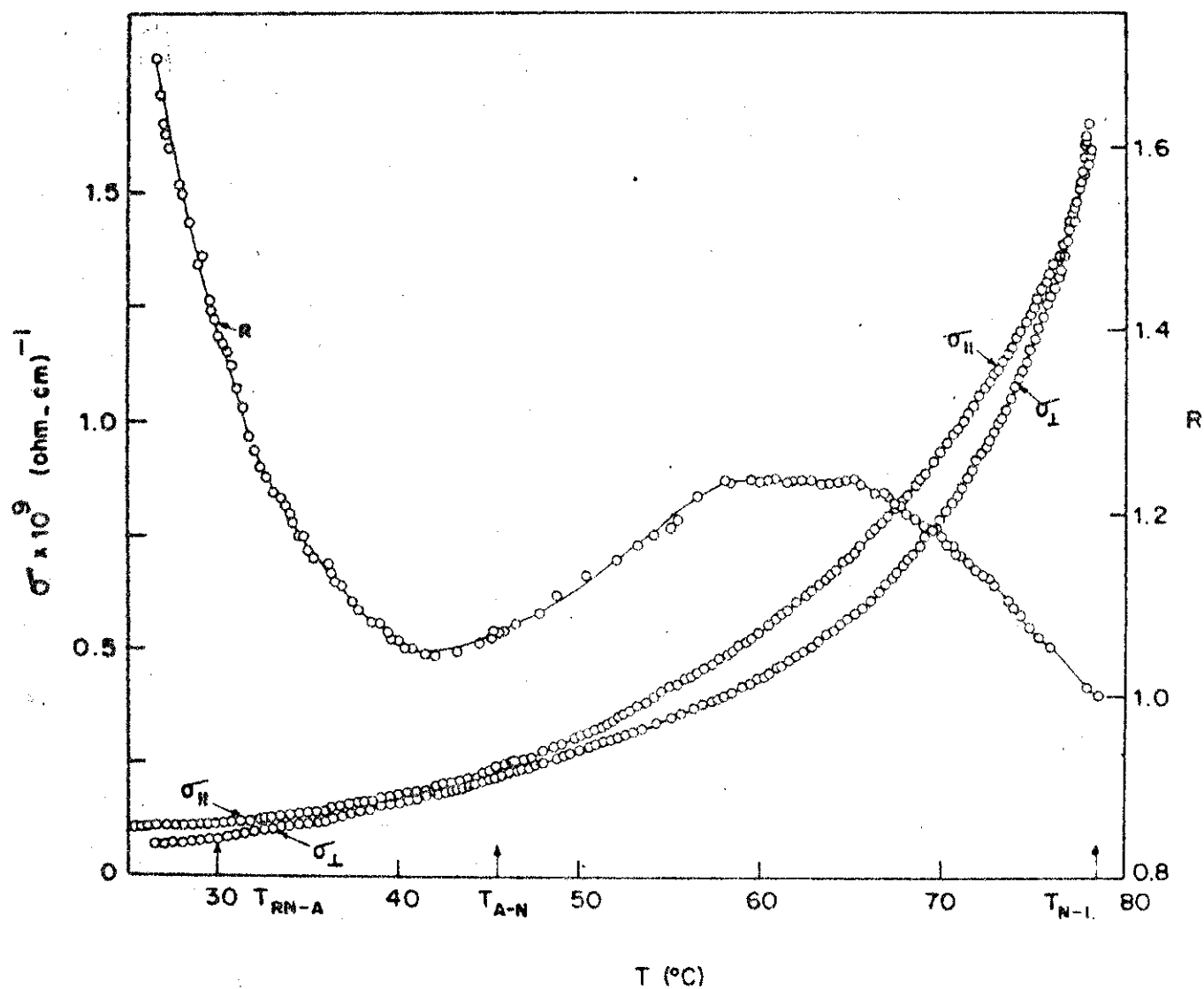


FIGURE 7.2:

The principal electrical conductivities $\sigma_{\parallel}$ and $\sigma_{\perp}$, and the ratio $R = \sigma_{\parallel}/\sigma_{\perp}$ of 6 OCB/8 OCB mixture as functions of temperature in the nematic, smectic A and re-entrant nematic phases.

perature and then begins to decrease. The decrease is rapid for most of the smectic range. The value of $\sigma_{||}$ reaches a minimum at about 85°C and then begins to increase. The rate of increase is faster near the smectic A - re-entrant nematic transition. $\sigma_{\perp}$ shows a monotonic decrease with the lowering of temperature.

The ratio of the electrical conductivities R has a value equal to 1 near T_{NI} . As the temperature is lowered, R increases throughout the normal nematic range, reaching a value nearly equal to 1.3 at a temperature very close to the smectic A-nematic transition point (T_{AN}).

With further decrease in temperature, R also decreases in the smectic A phase. Similar decreasing trends of R in the smectic A phase have been observed earlier for several bilayer compounds.⁷

The value of R continues to decrease till about the mid point of the smectic range where it attains a value nearly equal to 0.8. Beyond this R increases with further

cooling, the increase becoming very sharp as the re-entrant nematic-smectic A transition temperature (T_{RN-A}) is approached. This is clearly a pretransitional effect prior to the formation of the re-entrant nematic phase. Interestingly, the temperature at which R reverses its trend corresponds to the approximate temperature at which the mean dielectric constant $\bar{\epsilon}$ shows a change of slope (discussed in section 3 of chapter V). This is perhaps also related in some manner to the reversal in sign of the thermal expansion of the layer spacing discussed in chapter IV.

On approaching T_{RN-A} , the value of R increases very rapidly. The increasing trend continues even below T_{RN-A} , the value in the re-entrant nematic phase at the lowest temperature studied ($T_{RN-A} - T = 12^\circ\text{C}$) being about 16 (not shown in the figure 7.1).

(b) 6 OCB/8 OCB Mixture

While both $a_{||}$ and $a_{\perp}$ decrease with decrease of temperature, $a_{\perp}$ dips down further compared to $a_{||}$ in

the nematic range (figure 7.2). The nature of the variation of R is almost similar to that observed in 12 CPMBB. The value of R which increases on lowering the temperature from T_{NI} starts decreasing near T_{AN} . After reaching a minimum in the smectic phase, R increases near T_{RN-A} , the increase being less steep than that observed in 12CPMBB. The maximum value of R in the re-entrant nematic phase is nearly 1.8 at $T_{RN-A} - T = 2.1^\circ\text{C}$.

The interesting behaviour of R in both the systems is entirely due to the variation of $\sigma_{\perp}$. This is more obvious in 12 CPMBB. $\sigma_{\perp}$ exhibits the continuously decreasing trend over the entire temperature range. This indicates that only the ionic mobility normal to the layer gets affected with the approach of the re-entrant nematic phase and the consequent structural changes while the mobility along the layer remains practically unaffected. The sharp increase in R near T_{RN-A} shows that a nematic like behaviour is manifested as a pretransitional effect even in the smectic phase. This is more pronounced in the pure compound than in the mixture.

The fact that the value of R is much higher in the re-entrant nematic phase than in the normal nematic phase implies that there is some difference in the molecular associations between the two phases.

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