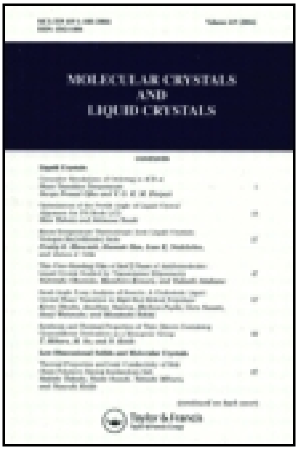

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Pre-Transitional Effects in the Electrical Conductivity of Re-Entrant Nematogens

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PRE-TRANSITIONAL EFFECTS IN THE ELECTRICAL CONDUCTIVITY OF RE-ENTRANT NEMATOGENS

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ABSTRACT. The principal electrical conductivities $\sigma_{\parallel}$ and $\sigma_{\perp}$ of mixtures of two eutectic compositions have been studied as functions of temperature and composition in the nematic, smectic A and re-entrant nematic phases. The conductivity ratio $\sigma_{\parallel}/\sigma_{\perp}$ shows strong pretransitional effects.

INTRODUCTION. In our earlier papers[1-4] we had shown that there is evidently no difference between the re-entrant nematic and the high temperature nematic phases, particularly regarding the static dielectric constants and the electrical conductivity. It was also shown that the electrical conductivity is a sensitive measure of smectic ordering as evidenced by the behaviour of the conductivity ratio $R = \sigma_{\parallel}/\sigma_{\perp}$. The value of R in the re-entrant nematic phase was found to be comparable with that of the high temperature nematic phase, except in the case of 4-cyanophenyl-3'-methyl-4(4'-dodecyloxy)benzoate[3] where in a very strong increase of R was found. This probably is due to the dielectric relaxation effects which start manifesting at rather low frequencies for this triaromatic compound. In this paper we re-

§Humboldt fellow, on leave of absence from the Raman Research Institute, Bangalore-560 080, India port the electrical conductivity studies of mixtures consisting of biaromatic cyano compounds. Because of the comparatively short molecular length, the influence of the dielectric relaxation should be diminished. Furthermore, we have used electrolyte dopants in the present experiments.

EXPERIMENTAL. The binary system used in the present study consists of two eutectic compositions A and B having three components each. Table I gives the fractions of these components calculated from the melting enthalpies and temperatures using the Schröder-van Laar equation and Table II gives the transition temperatures of the compositions A and B. The phase diagram of the compositions is shown in Fig.1. The basic composition A exhibits only a (normal) nematic phase while the composition B shows in addition both the smectic A and the re-entrant nematic phases. The re-entrant nematic phase is also exhibited by mixtures for concentrations higher than 53% by weight of B.

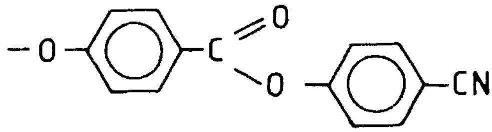
The electrical conductivities were measured for 4 different concentrations, viz, 25.1, 50.2, 60.8 and 75.1% by weight of B in A, in addition to the basic compositions A and B. The complex impedance of the magnetically aligned sample (thickness = 1 mm, B = 1 Tesla) was measured using an automatic Hewlett-Packard bridge (HP 4274 A) at a frequency of 100 Hz[5].

RESULTS. To start with, two different dopants, viz, N-dodecyl ethyldimethylammonium-4-hexyloxy benzoate (ZLI 235, Merck) and tetrabutylammonium-picrate (TBAP) were tried with a 60.8% weight mixture of B in A well as with tetrabutylammonium-picrate (TBAP). The Arrhenius plots of the electrical conductivity of the doped and undoped samples are given in Fig.2 while the conductivity ratio versus temperature plots of the same samples are given in Fig.3. It is seen that although the effect of both dopants is to increase the absolute value of σ (Fig.2), one of them, viz, TBAP, drastically reduces the sharpness of the R versus temperature curve (Fig.3). In contrast, the other dopant ZLI 235 does not alter the shape of the

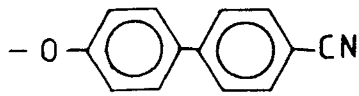
TABLE I

Molecular structure, melting enthalpies (ΔH/kJ·mol^{-1}) and melting points (t/^{o}C) determined by DSC, and mole fraction (x) of the components A and B

	A	B
	C_8H_{17}-	C_9H_{19}-
ΔH_m	40.6	45.2
t_m	70.9	75.9
x	0.157	0.134



	A	B
	C_7H_{15}-	C_8H_{17}-
ΔH_m	26.4	27.6
t_m	53.3	54.1
x	0.494	0.552



	A	B
	C_7H_{15}-	C_8H_{17}-
ΔH_m	22.6	28.1
t_m	71.9	72.7
x	0.349	0.314

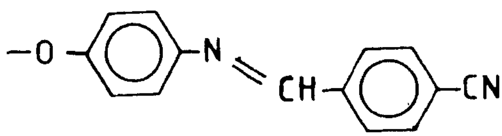


TABLE II

Transition temperatures of A and B

Transition	Temperature/^{o}C	
	A	B
isotropic-nematic	86.4	88.7
nematic - smectic A	-	70.6
smectic A - re-entrant nematic	-	20.2
calculated melting points	31.2	36.0
experimental melting points	32.0	35.4

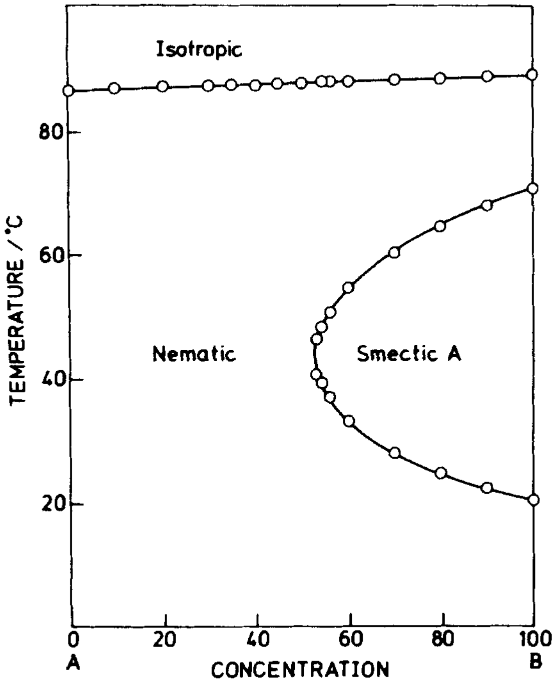


Figure 1. Phase diagram of the eutectic compositions A and B. Concentration is given in weight percent of B in A.

curve significantly and hence was used for all the mixtures studied. From a plot of log σ versus log f, we have estimated that for all mixtures doped with ZLI 235, the influence of the dielectric loss on the electrical conductivity measured at 100 Hz is less than 2%.

The plots of R versus temperature are shown in Fig.4 for different compositions of B in A. Remarkably, the shape of the curves do not differ for the smectic mixtures and the non-smectic ones. Starting from the clearing point, as the temperature is decreased R initially shows an increase but soon reverses its trend, evidently due to the influence of short range smectic order which causes a decrease of $\sigma_{\parallel}$. R continues its decreasing trend right through the smectic A - nematic

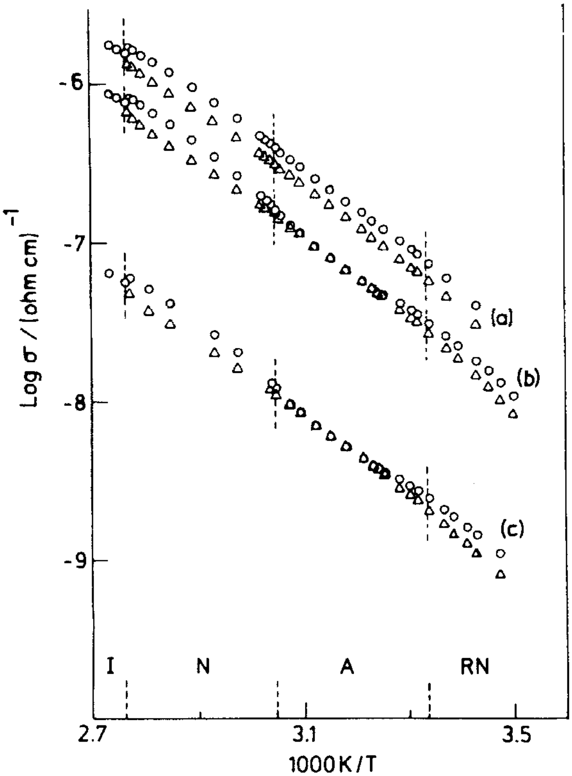


Figure 2.

Plot of log σ versus 1/T for the 60.8% weight mixture of B in A. (a) doped with TBAP, (b) doped with ZLI 235, (c) undoped

transition and attains a minimum value around the middle of the smectic region. On further decrease of temperature, R starts exhibiting an increasing trend which is continued right upto the lowest temperature in the re-entrant nematic phase, no discontinuity in R being observed a the re-entrant nematic - smectic A transition either. Obviously, when cooling beyond the middle of the smectic range, the smectic order becomes unstable again. The minimum of the conductivity ratio, which indicates the maximum smectic stability, occurs at about 40^{o}C for all compositions. It is worth noting that a minimum in R is observed even for the non-smectic basic composition A, although none of the constituent components exhibits a smectic phase.

The results of electrical conductivity studies show large pretransitional effects not only versus temperature, but also versus composition. Especially with respect to the maximum

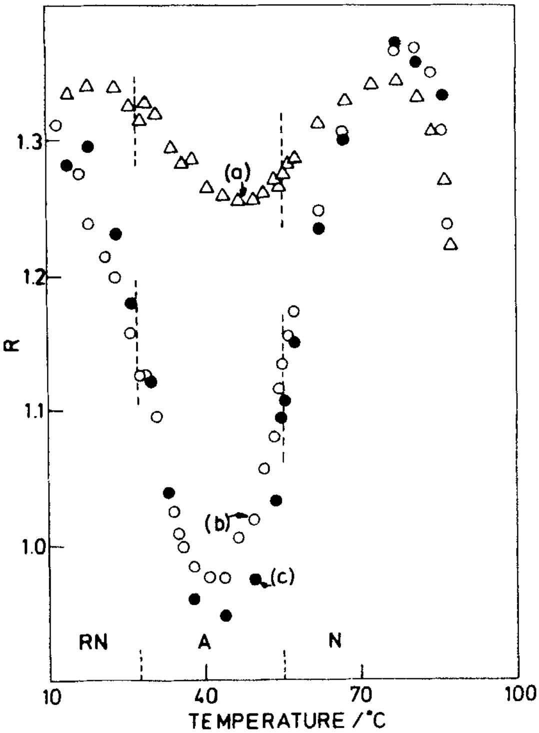


Figure 3. Electrical conductivity ratio R vs temperature for the doped and undoped samples of the 60.8% weight mixture of B in A. (see legend of Fig.2).

smectic stability found for the non-smectic mixture A, it should be of interest to see if other physical properties, e.g. elastic constants, also show a similar behaviour.

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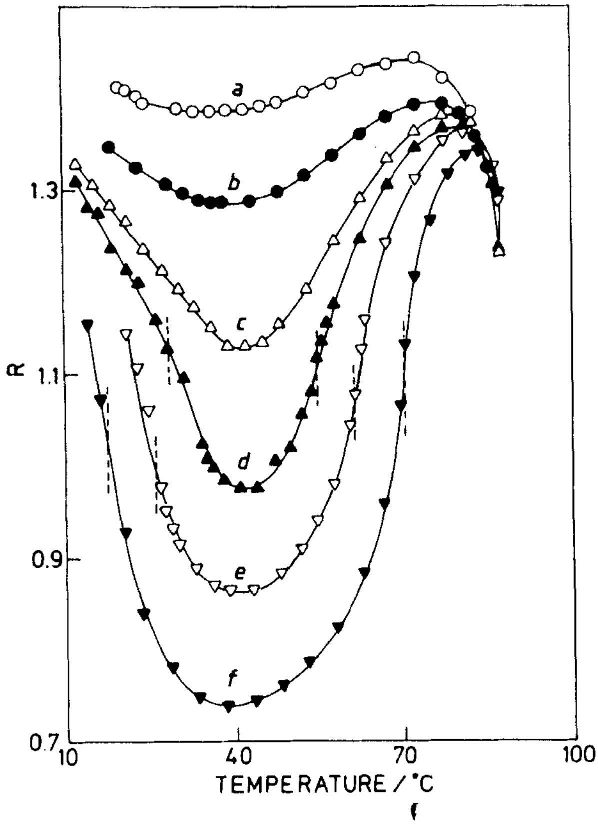

Figures 4. Coductivity ratio R vs temperature curves for mixtures of B in A. The weight concentrations studied are (a) 0% (ie A), (b) 25.0%, (c) 50.2%, (d) 60.8%, (e) 75.1% and (f) 100% (ie B).

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