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Optical birefringence studies of a binary mixture with the nematic–smectic A_d -re-entrant nematic phase sequence

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Abstract

We report the measurements of birefringence as a function of temperature of a binary system 4-cyanophenyl [4'(4''-n-heptylphenyl)]benzoate (7CPB) + 4-cyanophenyl 4-nonylbenzoate (9.CN) showing a nematic–smectic A_d -re-entrant nematic phase sequence by means of the optical transmission method. The temperature dependence of the birefringence has been determined from the transmitted intensity data and the orientational order parameters have been calculated. These observations indicate that re-entrant nematic to induced smectic A_d and induced smectic A_d to nematic phase transitions for all the mixtures are of second order. There is a continuous change in the Δn values at the nematic–smectic A_d and smectic A_d -re-entrant nematic phase transitions. However, for some mixtures a slight increase in birefringence on cooling in the vicinity of the smectic A_d -re-entrant nematic transition has been observed. We have also fitted our experimental results with those calculated from the modified McMillan theory as proposed by Luckhurst and Timimi.

1. Introduction

Binary mixtures of nematic liquid crystals containing molecules with strongly polar end groups are known to exhibit a novel phase diagram with induced smectic islands surrounded by a nematic sea, i.e. both the induced smectic and re-entrant nematic phases appear simultaneously in such mixtures [1–3]. In our earlier paper [4] we have reported the phase diagram and the results of x-ray diffraction measurements of the binary mixtures of 4-cyanophenyl [4'(4''-n-heptylphenyl)] benzoate (7CPB) + 4-cyanophenyl 4-nonylbenzoate (9.CN). The characteristic features of this phase diagram are that, although we observe a monotropic re-entrant nematic phase in the concentration range $0.4 < x_{9.CN} < 0.8$, for a small composition range $0.8 < x_{9.CN} < 0.87$, the re-entrant nematic phase appears well ahead of the melting temperature. To understand the formation of the induced smectic and re-entrant nematic phases, we have studied the physical properties of this mixture at seven different compositions. Since the order parameter is one of the most important material properties of liquid crystals, several methods for its determination have been developed. Of these, the widely accepted view is that the data obtained from optical

and diamagnetic susceptibility measurements are more precise, since these methods involve fewer approximations as far as the relative orientation of the long molecular axis is concerned. Optical transmission methods have been used to determine the temperature dependences of the optical birefringence, Δn , which provides a macroscopic measure of the anisotropy of the liquid crystalline phase and can also be considered as a measure of the orientational order parameter $\langle P_2 \rangle$. From optical birefringence studies, both the orientational order parameter as well as the nature of the nematic–smectic A_d and smectic A_d to re-entrant nematic phase transitions have been assessed in this work. We have also fitted our experimental order parameter values with those calculated from the modified McMillan model as proposed by Luckhurst and Timimi [5].

2. Experimental details

The compounds 7CPB and 9.CN were purchased from AWAT Co. Ltd, Warsaw, Poland and were used without further purification. The structural formulae and chemical names of the pure compounds are as follows.

Component 1: (4-cyanophenyl [4'(4''-n-heptylphenyl)]) (abbreviated to 7CPB)

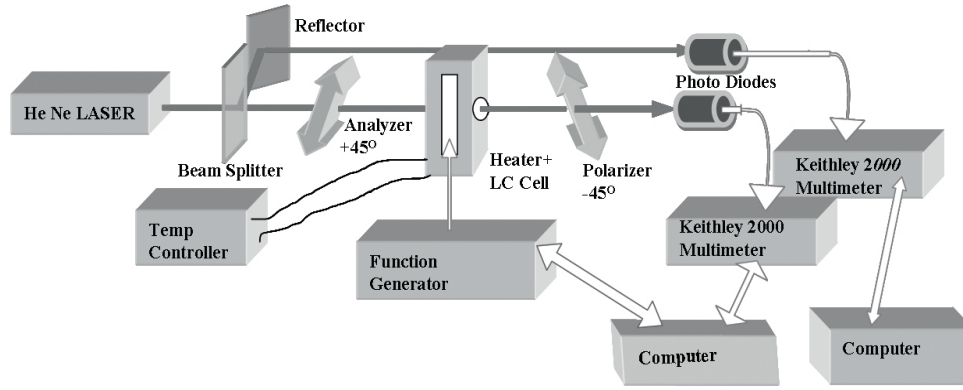
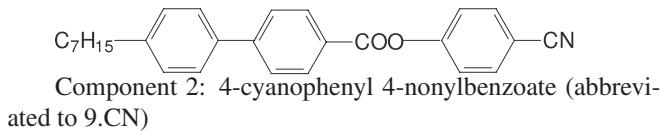


Figure 1. Schematic diagram of the experimental set-up for birefringence measurement.



Seven mixtures having molar concentrations $x_{9,CN} = 0.176, 0.417, 0.471, 0.559, 0.662, 0.774$ and 0.827 were prepared. Polarizing microscopy observations and x-ray diffraction measurements of these mixtures have already been reported by us earlier [4].

2.1. Optical birefringence measurements

The block diagram of the experimental set-up is shown in figure 1. An He–Ne laser ($\lambda = 632.8$ nm) beam was directed onto a homogeneously aligned (planar) ITO-coated liquid crystal cell of thickness $8.9 \mu\text{m}$ (purchased from AWAT Co. Ltd, Warsaw, Poland) which was placed between two crossed linear polarizers. The temperature of the cell was regulated and measured with a temperature controller (Eurotherm PID 2216e) with an accuracy of $\pm 0.1^\circ\text{C}$ by placing the cell in a brass thermostat. During the experiment the temperature was varied at a rate of 0.5 K min^{-1} and the transmitted light intensity was measured by a photodiode at an interval of 12 s. The stability of the laser intensity was monitored by another identical photodiode. The photodiode outputs were measured by precision multimeters (Keithley model 2000). The transmitted light intensity was measured as a function of temperature in the planar aligned sample (figure 1). A function generator can be used to apply a 1 kHz sinusoidal voltage of magnitude much higher than the Fredericksz threshold voltage of the sample under investigation. Thus, for a positive dielectric anisotropy material, the application of such an electric field to the planar cell results in a homeotropic alignment of the sample. The study of the transmitted light intensity in this geometry can be used as a preliminary test of the existence of tilted phases [6, 7]. However, in this work, we have found the existence of only orthogonal phases in all the mixtures.

The intensity of the transmitted laser light can be written as [8]

$$I_t = \frac{\sin^2 2\theta}{2} (1 - \cos \Delta\varphi) \quad (1)$$

where θ is the angle made by the polarizer with the optical axis and the phase difference

$$\Delta\varphi = \frac{2\pi}{\lambda} \Delta n d \quad (2)$$

$\Delta n = n_e - n_o$, where n_e and n_o are the extraordinary and ordinary refractive indices of the liquid crystal medium, and d is the sample thickness. The angle θ is set at 45° to optimize the measurements. The birefringence is calculated from the measured intensity [8, 9]. The outputs of the digital multimeters and the temperature controller were interfaced with a computer and the measurements were performed using a suitable program.

In the present study, the birefringence, Δn , has been measured from the transmitted intensity from a cell of thickness $8.9 \mu\text{m}$ using equations (1) and (2). In order to get an estimate of the precision of our experimental set-up, we have also determined the refractive indices of one pure sample (9.CN) by the thin prism technique [10–12]. The values of Δn determined from the transmission method are found to be about 4% higher than those measured by the thin prism method. Such a higher value of Δn from the transmission method of thin samples has also been reported by others [13].

3. Results and discussion

3.1. Phase diagram

Figure 2 shows the phase diagram of the binary system 7CPB + 9.CN as observed by us from polarizing optical microscopy. The induced smectic A_d phase appears in the phase diagram in the shape of an elliptical island within the concentration range $0.4 < x_{9,CN} < 0.87$, surrounded by a nematic sea, i.e. the induced smectic and re-entrant nematic phases appear simultaneously in such mixtures. In some cases, the re-entrant nematic phase is suppressed due to solidification. Moreover, for a certain concentration range (near the eutectic point $x = 0.85$), the re-entrant nematic phase appears well ahead of the onset of the melting temperature.

3.2. Birefringence measurements and the orientational order parameter

Figure 3 shows the comparison between the experimentally determined values of the birefringence ($\Delta n = n_e - n_o$)

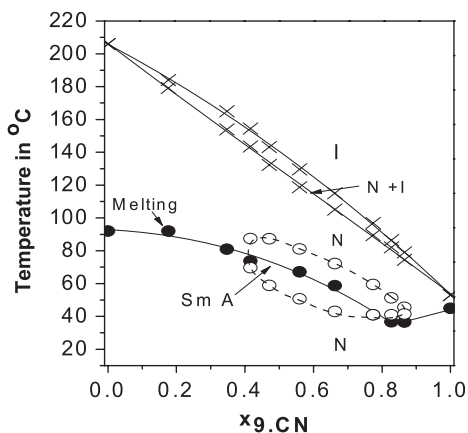


Figure 2. Phase diagram for the binary system of 7CPB + 9.CN. x is the mole fraction of 9.CN. I isotropic; (I + N) nematic–isotropic coexisting region; Sm smectic phase, N nematic phase.

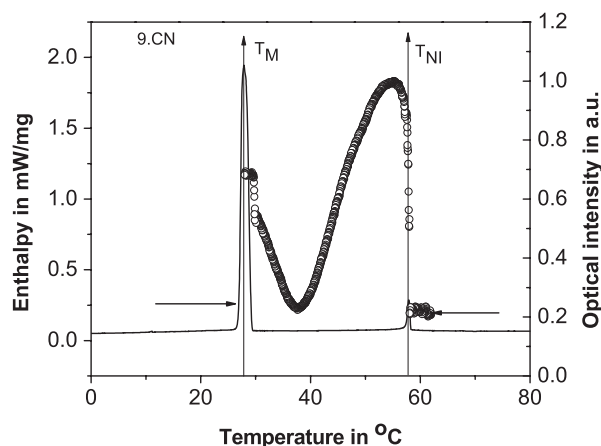


Figure 4. DSC thermogram (—) and transmitted intensity (O) as a function of temperature during heating of 9.CN (DSC scan rate $2^{\circ}\text{C min}^{-1}$).

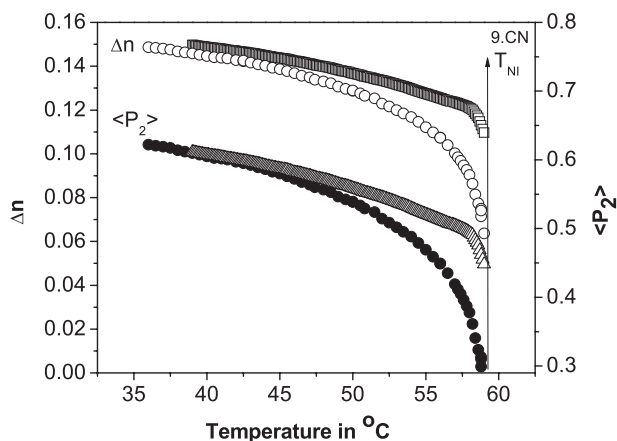


Figure 3. Temperature dependence of Δn and $\langle P_2 \rangle$ for pure sample 9.CN. \square data for Δn measured from optical transmission method; \circ data for Δn measured from thin prism method; \triangle data for $\langle P_2 \rangle$ measured from optical transmission method; \bullet data for $\langle P_2 \rangle$ measured from thin prism method.

from refractive index measurements of one of the pure components (9.CN) by optical transmission as well as the thin prism technique. Also shown in the same figure is the temperature dependence of the orientational order parameter $\langle P_2 \rangle$. The values of Δn and $\langle P_2 \rangle$ in the transmission method are found to be about 4% and 1% higher, respectively, than those measured by the thin prism method. Both the optical birefringence Δn and the orientational order parameter values $\langle P_2 \rangle$ as determined from the thin prism method are observed to decrease rapidly at the nematic–isotropic phase transition. However, Δn and $\langle P_2 \rangle$ values determined from the optical transmission method are relatively higher near the nematic–isotropic transition temperature.

The possible reason for the obvious discrepancy in the two sets of measurements near the transition is due to the fact that in thin prisms the sample thickness is very much higher (20–40 times) than the $8.9 \mu\text{m}$ cell which is used in the transmission method. Therefore, the surface anchoring (which is much better for the thin cells) retains the monodomain alignment

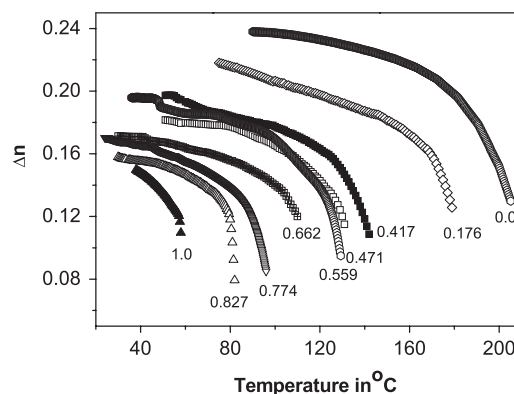


Figure 5. Birefringence ($\Delta n = n_e - n_o$) as a function of temperature for different mixtures and pure compounds. Mole fractions of different mixtures are indicated in the figure.

right up to the nematic–isotropic transition in comparison to the bulk samples in the thin prism. Such a higher value of Δn from the transmission method of thin samples has been reported by others [13]. It is to be noted here that the optical transmission method is an excellent system for identification of the phase transition temperature, especially if the phase transition is not truly of second order. Again, this method can also be used to identify the presence of tilted phases in the liquid crystalline system by studying the transmitted intensity for both the planar and homeotropic aligned cell [6, 7]. Figure 4 shows the temperature dependence of the optical intensity for the pure sample 9.CN. The DSC data for the same sample is also included for comparison. It is clearly seen that the melting and N–I transition temperatures are distinguishable from the transmission method.

The temperature variation of optical birefringence values for different mixtures as a function of temperature is shown in figure 5. The birefringence values of 7CPB are higher than those obtained from 9.CN. This is expected because 9.CN contains two phenyl rings in the rigid core whereas the 7CPB molecule contains three benzene rings in its core. As expected, the addition of one aromatic benzene ring leads to an increase

in the anisotropy of 7CPB. In mixtures, Δn values are found to decrease with the increase in mole fraction of 9.CN. There is no discontinuity in the Δn values at the N_{re} – SmA_d as well as SmA_d – N transition temperatures. These observations indicate that re-entrant nematic to induced smectic A_d and induced smectic A_d to nematic phase transitions for all the mixtures are of second order. High resolution DSC measurements have also been done. Since the order of transition is second order no peak was detected at the SmA_d – N and SmA_d – N_{re} transitions [4].

It should be noted that, in spite of the continuous change in the birefringence values between the N and N_{re} phases, separated by the SmA_d gap, we have observed only a slight increase in birefringence on cooling in the vicinity of the SmA – N_{re} transition in some mixtures. However, Chen *et al* [14] have observed somewhat of an increase in the birefringence at the N – SmA_d transition and an overall decrease in the birefringence at the SmA_d – N_{re} transition in a binary system of 6OCB and 8OCB, showing induced smectic A_d and re-entrant nematic phases.

In this work we are using a simple procedure for the determination of the order parameter from birefringence measurements. In case of a uniaxial liquid crystalline phase, the temperature dependence of the birefringence is fitted to the following form:

$$\Delta n = \Delta n_0 \left(1 - \frac{T}{T^*}\right)^\beta \quad (3)$$

where Δn_0 , T^* and β are adjustable parameters. T^* is about 1–3 K higher than the clearing temperature and the exponent β depends on the molecular structure and its value is close to 0.2. This procedure enables us to extrapolate Δn to absolute zero temperature, Δn_0 [15].

The temperature-dependent birefringence is related to the order parameter as [16]

$$\langle P_2 \rangle = \frac{\Delta n}{\Delta n_0} \quad (4)$$

where Δn_0 is the birefringence in the completely ordered state, which was obtained from Haller's approximation for the order parameter (equation (3)).

It is to be noted that the typical procedure for the evaluation of the long range order parameter from the optical method requires the measurement of both the ordinary and extraordinary refractive indices as well as the density data. In such cases, using these three measured quantities, either the standard Vuks isotropic model [17] or Neugebauer's relations based on the anisotropy of the internal field [18] are adopted to determine the principal polarizabilities parallel and perpendicular to the molecular long axes, and hence the anisotropy of the molecular polarizabilities ($\Delta\alpha$) can be calculated. The normalized polarizability ($\Delta\alpha_0$) for a perfectly ordered crystal is determined from the well-known Haller extrapolation procedure and the order parameter is calculated from the ratio $\frac{\Delta\alpha}{\Delta\alpha_0}$. According to de Jue [16], the variation of density (ρ) over the nematic range is usually small and the temperature dependence of Δn gives a good indication of the variation of the order parameter with temperature. Kuczynski

et al [19] have also shown that the order parameter determined directly from birefringence measurements is consistent with the $\langle P_2 \rangle$ values calculated from the polarizability data.

Since most of the mixtures studied in this system have two nematic phases and one smectic phase, the temperature variation of Δn is different for different phases; therefore we have fitted equation (3) by taking the values of Δn only in the higher temperature nematic phase [20–23].

Our experimental order parameter values calculated from equations (4) are shown in figure 6. It is observed that for all the mixtures the temperature dependence of the order parameter in N_{re} and N phases is quite pronounced in comparison to those in the smectic A_d phase. These values are found to vary continuously across the N – SmA_d and SmA_d – N_{re} phase transitions, indicating second-order phase transitions.

Our order parameter values for both the pure compounds (figures 6(a) and (b)) do not agree well with Maier–Saupe theory [24]. However, for the mixture $x = 0.176$ (figure 6(c)), where only the nematic phase exists, the agreement with theory is quite good. The order parameters have been fitted to those calculated from McMillan's theory [25, 26]. The single-particle McMillan potential is given by

$$\varepsilon(\cos \theta, z) = -\varepsilon_0[\delta\alpha\tau \cos(2\pi z/d) + \{\eta + \alpha\sigma \cos(2\pi z/d)\}P_2(\cos \theta)] \quad (5)$$

where α and δ are two adjustable parameters, z is the displacement along the layer normal, d is the layer thickness, $\eta = \langle P_2(\cos \theta) \rangle$, the orientational order parameter, while $\tau = \langle \cos(2\pi z/d) \rangle$ is the translational order parameter and $\sigma = \langle P_2(\cos \theta) \cos(2\pi z/d) \rangle$ is the mixed translational and orientational order parameter. The parameter ε_0 is obtained from the nematic/isotropic transition temperature, assuming the simple mean-field theory result ($kT_{NI}/\varepsilon_0 = 0.22019$). The values of η , τ and σ are calculated using the self-consistency relationships as a function of temperature for various values of the parameters α and δ . In the calculation using McMillan's model, the parameter α , which varies with the chain length, has been varied keeping the parameter δ , (which is the ratio of the translational to the orientational part of the potential) fixed ($\delta = 0.16$). The best fitted theoretical curve and the values of α used for this calculation are shown in figures 6(d)–(i). The agreement between the experimental $\langle P_2 \rangle$ values from the birefringence measurements with those calculated from McMillan's theory is poor for all the mixtures. In order to improve this disagreement, we have compared our $\langle P_2 \rangle$ values with those calculated from the modified McMillan theory as proposed by Luckhurst and Timimi [5]. Since in the binary system under study there exist both homo- and heterodimers, the parameter α is expected to be weakly temperature-dependent. Therefore by suitably varying α with temperature, we obtained a situation where lowering the temperature still produces the usual SmA – N transition. However, further decrease in temperature reduces α to such an extent that the SmA phase becomes unstable and reverts to a nematic phase, or in other words a re-entrant nematic phase is formed [4].

We are able to obtain a re-entrant nematic phase by using an essentially linear temperature variation of α . Using

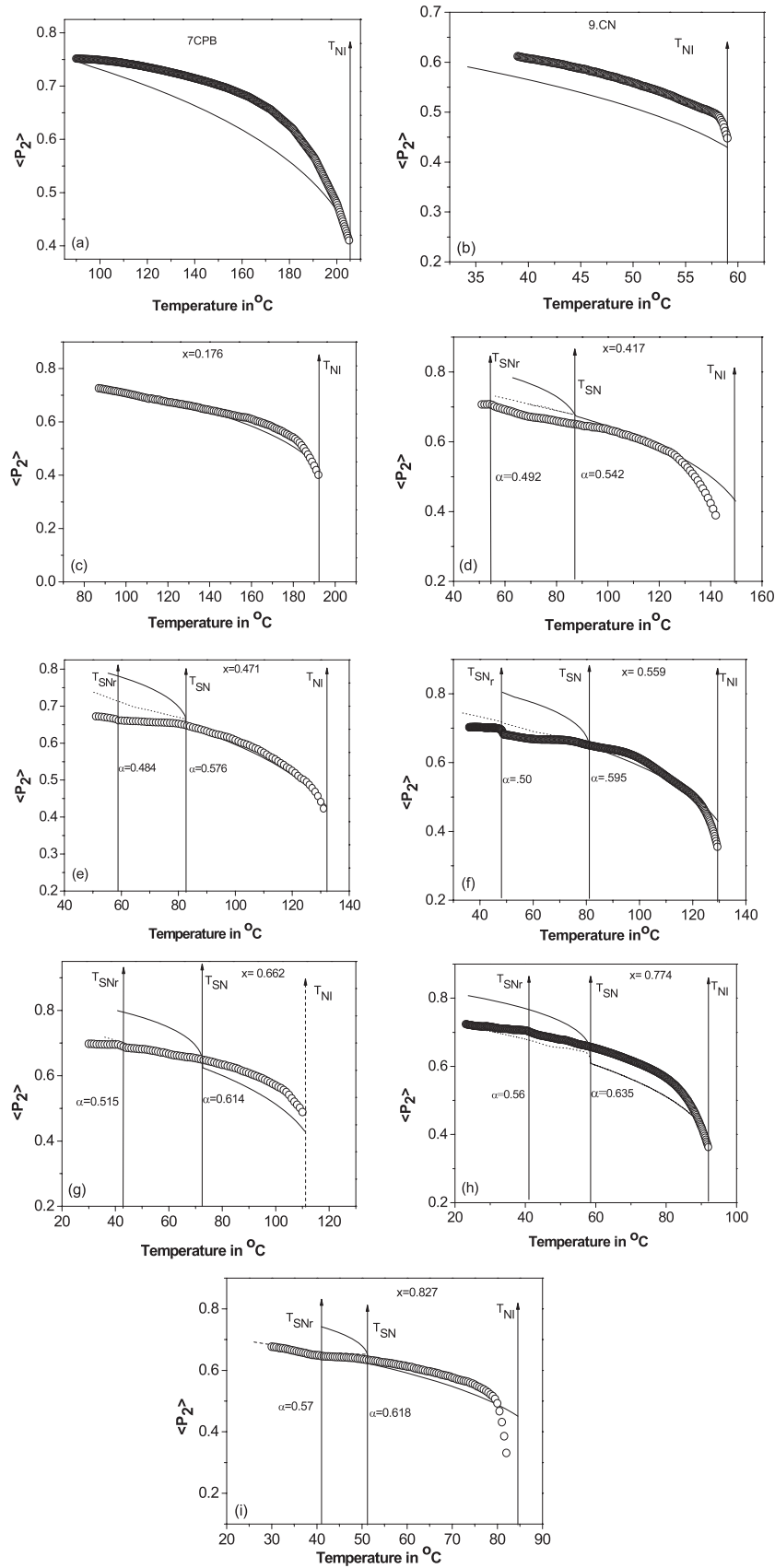


Figure 6. Temperature variation of $\langle P_2 \rangle$ for (a) 7CPB, (b) 9.CN, (c) $x = 0.176$, (d) $x = 0.417$, (e) $x = 0.471$, (f) $x = 0.559$, (g) $x = 0.662$, (h) $x = 0.774$ and (i) $x = 0.827$, $O = \langle P_2 \rangle$ from birefringence measurement — $\langle P_2 \rangle$ from Maier–Saupe theory ((a)–(c)), from McMillan’s theory ((d)–(i)), $\cdots \cdots \langle P_2 \rangle$ from modified McMillan theory by Luckhurst and Timimi. T_{NI} = nematic–isotropic, T_{SN} = smectic A_d –nematic and T_{SNr} smectic A_d –re-entrant nematic phase transition temperatures. Within the smectic phase, the change in α values required to fit experimental data is shown in the respective figures.

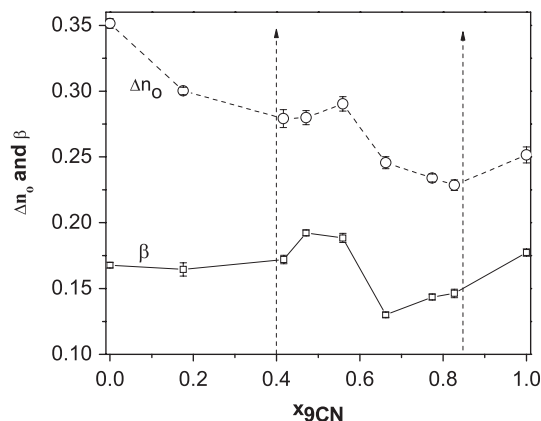


Figure 7. Extrapolated birefringence at absolute zero temperature (Δn_0) and exponent β plotted as a function of mole fraction of 9.CN. Vertical bars indicate estimated error.

this variation of α and setting δ equal to 0.16 we have obtained the dependence of the orientational order parameters with temperature which are also shown in figures 6(d)–(i). The agreement between the experimental $\langle P_2 \rangle$ values from birefringence measurements with those calculated from the modified McMillan theory is very good for all the mixtures, particularly for those mixtures showing both induced smectic and re-entrant nematic phases. Both SmA_d –N transitions are predicted to be second order by this model and this prediction is also in agreement with the DSC measurement [4], where no change in the transition enthalpies are observed at the re-entrant nematic to smectic A_d as well as smectic A_d to nematic phase transitions.

In figure 7 we have plotted the birefringence values extrapolated to absolute zero (Δn_0) and exponent β as a function of the mole fraction of 9.CN. It is found that Δn_0 values are greater in the lower concentration region of 9.CN and decreases gradually with the increase in mole fraction of 9.CN. However, it shows local maxima near equimolar concentration. The β values of both the pure compounds are nearly the same. The variation of β also shows local maxima near equimolar concentration. It may not be out of place to mention that the variation of layer thickness with concentration shows a maximum near the same concentration range as observed by us earlier [4]. As the anisotropy is almost proportional to the apparent molecular length (molecular width being constant) our x-ray result does support the local maximum of Δn_0 .

Figure 8 shows the variation of $\langle P_2 \rangle$ values with the mole fraction of 9.CN at $T = T_{\text{SN}} - 5^\circ\text{C}$, where all the mixtures show a smectic phase. It is observed that the OOPs in the smectic phase show a definite minimum at around $x = 0.5$, which corroborates the findings of the x-ray diffraction measurements done on this system [4]. This minimum in the order parameter values is attributed to specific interactions between the molecules, which, in trying to pack the different molecules within the layers of the smectic A_d phase, in effect, reduces the orientational free volume within the layers. This observation is very similar to polar–non-polar systems showing an induced smectic A_d phase [10–12]. This lowering in the

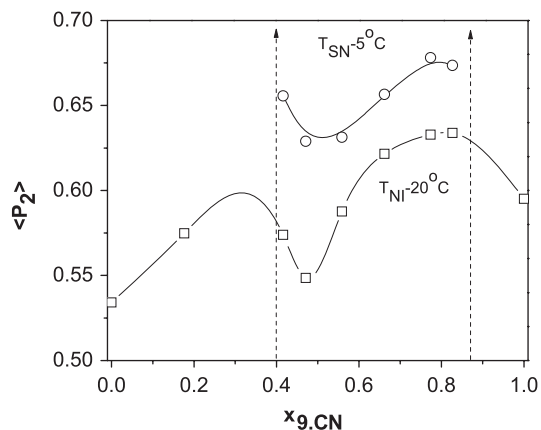


Figure 8. Concentration dependence of $\langle P_2 \rangle$ within the nematic phase at $T_{\text{NI}} - 20^\circ\text{C}$ and smectic phase at $T_{\text{SN}} - 5^\circ\text{C}$.

order parameter values has also been found in the nematic phase of this system.

4. Conclusions

Optical transmission studies have been undertaken to measure the birefringence of a binary system of nematogenic compounds exhibiting induced smectic A_d and re-entrant nematic phases. A simple and precise method for the determination of the optical birefringence as a function of temperature was used in this work. It was possible to measure the birefringence Δn with reasonably good accuracy (better than $\pm 10^{-4}$) in all the liquid crystalline phases. No discontinuity has been observed in the Δn values at the N_{re} – SmA_d as well as SmA_d –N transition temperatures. These observations indicate that the re-entrant nematic to induced smectic A_d and induced smectic A_d to nematic phase transitions for all the mixtures in this system are of second order. In spite of the continuous change in the birefringence values between the N and N_{re} phases, separated by the Sm A_d gap, we have observed a slight increase in birefringence on cooling in the vicinity of the Sm A_d – N_{re} transition for some mixtures. The agreement between the experimental $\langle P_2 \rangle$ values from the birefringence measurements with those calculated from McMillan's theory have been found to be poor in the smectic A_d phase. This discrepancy has been removed by recalculating the orientational order parameter values according to a modified McMillan theory as proposed by Luckhurst and Timimi, taking into account a slight temperature dependence of the α parameter. Both N– SmA_d and Sm A_d – N_{re} phase transitions, which are predicted to be of second order by this model, are also found to be in agreement with our birefringence as well as DSC measurements [4].

Acknowledgments

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