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Effect of a rigid, non-polar solute on the dielectric anisotropy, the splay and bend elastic constants, and on the rotational viscosity coefficient of 4-4′-*n*-heptylcyanobiphenyl

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The effect of mixing a rigid, non-polar, non-mesogenic solute, biphenyl (C_6H_5–C_6H_5), in the nematic solvent 7CB (4,4′-*n*-heptylcyanobiphenyl) is investigated. The solute is found to reduce the nematic order and a two-phase region appears. We report measurements of the transition temperatures, dielectric anisotropy, and splay and bend elastic constants, as well as the rotational viscosity coefficient by the method of electric field-induced Fréedericksz transition for biphenyl concentrations up to 8.0%.

1. Introduction

Non-mesomorphic solutes in general depress the normal nematic–isotropic transition temperature in liquid crystals and it has been seen that the presence of such impurities leads to the formation of a two phase region [1–3]. This is consistent with the laws of thermodynamics and the first order nature of the nematic–isotropic transition. In an earlier communication [4] we reported the effect of the rigid, non-polar, non-mesogenic solute 'biphenyl' on the transition temperatures of both the smectic–nematic (T_{AN}) as well as the nematic–isotropic transitions (T_{NI}), the dielectric anisotropy, the splay and bend elastic constants and the rotational viscosity coefficient of 4,4′-*n*-octylcyanobiphenyl (8CB) which has both nematic as well as smectic phases. In the 8CB + biphenyl system anomalous behaviour of both the splay elastic constant K_{11} and the dielectric anisotropy $\Delta\varepsilon$ were observed near the N–SmA transition. Later we carried out another set of experiments near the N–SmA transition and reported the results in an attempt to explain these anomalies [5]. The interesting results obtained in the case of the 8CB + biphenyl system led us to study the effect of biphenyl on 7CB. Incidentally, pure 7CB unlike 8CB has no smectic phase. Consequently the possible effects of the presence of a smectic phase on the nematic order does not arise. Here we have concentrated entirely on the nematic–isotropic transition of 7CB and taken a closer look at the biphenyl-induced two-phase region near the N–I transition.

7CB is known to exhibit a first order N–I transition. We have observed that biphenyl is easily miscible with 7CB and lowers T_{NI} by an amount which depends on the concentration of added impurity. The effect of this rod-like non-polar impurity on the dielectric anisotropy, the Frank elastic constants (splay and bend) and on the effective rotational viscosity coefficient of pure 7CB is reported here. The experiments we have carried out involve electric field-induced Fréedericksz transition. The dielectric anisotropy and the Frank elastic constants are extracted from a set of measurements of the voltage dependence of capacitance of a sample cell filled with the 7CB plus biphenyl mixture. A method based on dynamic Fréedericksz transition is used for the determination of the rotational viscosity coefficient.

2. Details of the experimental method

We used a Hewlett-Packard LCR meter HP 4274A to measure the capacitance of the sample cell. The voltage was varied from 0.1 to 5.0 V at a frequency of 1 kHz. The sample cells, which were of very high precision, were obtained from Displaytech, USA. They consisted of two ITO coated glass plates with a spacing of 4.0 μm, and an active area of 0.26 cm^2, and underwent rubbed polyimide treatment to ensure planar orientation; the pretilt angle was quoted by the manufacturers to be less than 0.1°. The polyimide layer was deposited with gamma butyrol lactone. To minimize fringe electric fields a guard ring was incorporated. The temperature of the cells was controlled to within ±0.1 K with a Mettler hot stage FP 82. To study the textures of the samples a Leitz polarizing microscope was used. Both 7CB as well as biphenyl were obtained from Merck and were used without further purification.

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The samples used were mixtures of various concentrations of biphenyl, ranging from 1.0 to 8.0%, in pure 7CB. By studying the texture of the samples with the polarizing microscope, the nematic to isotropic transition temperatures were determined. In the capacitance measurement experiments the probe voltage of the LCR meter HP 4274A provided the aligning a.c. electric field. The voltage was varied from 0.1 to 5.0 V at a frequency of 1 kHz in the C_P–G mode of the instrument. In the neighbourhood of Fréedericksz transition readings were taken at intervals of 10 mV. The samples were filled in the cells and the C–V variation recorded for a large number of temperatures. All measurements were carried out by starting from the isotropic phase and then gradually cooling the sample to the nematic phase. The measurements were repeated by heating the sample from the nematic phase up to the isotropic phase. The two sets of measurements were seen to be in agreement.

The splay elastic constant K_{11} is related to the Fréedericksz threshold voltage V_{th} by the relation

$$K_{11} = \frac{\varepsilon_0 \Delta\varepsilon}{\pi^2} V_{\text{th}}^2 \tag{1}$$

where ε_0 is the permittivity of free space and $\Delta\varepsilon = \varepsilon_\parallel - \varepsilon_\perp$ is the dielectric anisotropy of the sample. The method of determination of $\Delta\varepsilon$ is described below.

The exact relationship between the cell capacitance C and the voltage V applied across the cell was obtained by Gruler *et al.* [6]. They showed that

$$\frac{V}{V_{\text{th}}} = \frac{2}{\pi}(1+\gamma\sin^2\phi_{\text{m}})^{1/2} \times \int_0^{\phi_{\text{m}}} \left[\frac{(1+\kappa\sin^2\phi)}{(1+\gamma\sin^2\phi)(\sin^2\phi_{\text{m}}-\sin^2\phi)}\right]^{1/2} \mathrm{d}\phi \tag{2}$$

and

$$\frac{C}{C_\perp} = \frac{\displaystyle\int_0^{\phi_{\text{m}}} \left[\frac{(1+\kappa\sin^2\phi)(1+\gamma\sin^2\phi)}{(\sin^2\phi_{\text{m}}-\sin^2\phi)}\right]^{1/2} \mathrm{d}\phi}{\displaystyle\int_0^{\phi_{\text{m}}} \left[\frac{(1+\kappa\sin^2\phi)}{(1+\gamma\sin^2\phi)(\sin^2\phi_{\text{m}}-\sin^2\phi)}\right]^{1/2} \mathrm{d}\phi} \tag{3}$$

where $\kappa = K_{33}/K_{11} - 1$ (K_{33} being the bend elastic constant), $\gamma = \varepsilon_\parallel/\varepsilon_\perp - 1$, ϕ is the tilt angle made by the director with a direction parallel to the cell walls, ϕ_{m} is the tilt angle at the centre of the cell and $C_\perp$ is the capacitance of the cell when the liquid crystal molecules are homogeneously aligned, that is, before the onset of Fréedericksz transition when the voltage applied is lower than the threshold voltage. These equations can be combined to yield

$$\frac{C-C_\perp}{C_\perp} = \gamma - \frac{2\gamma}{\pi}(1+\gamma\sin^2\phi_{\text{m}})^{1/2}\frac{V_{\text{th}}}{V} \times \int_0^{\sin\phi_{\text{m}}} \left[\frac{(1+\kappa x^2)(1-x^2)}{(1+\gamma x^2)(\sin^2\phi_{\text{m}}-x^2)}\right]^{1/2} \mathrm{d}x. \tag{4}$$

When the applied voltage is much higher than the threshold voltage, the director at the centre of the cell becomes perpendicular to the cell walls and $\phi_{\text{m}} = \pi/2$. Then the above equation reduces to

$$\frac{C-C_\perp}{C_\perp} = \gamma - \frac{2\gamma}{\pi}(1+\gamma)^{1/2}\frac{V_{\text{th}}}{V}\int_0^1 \left[\frac{(1+\kappa x^2)}{(1+\gamma x^2)}\right]^{1/2} \mathrm{d}x \tag{5}$$

or dividing by γ

$$\frac{C-C_\perp}{C_\parallel - C_\perp} = C_{\text{R}} = 1 - \frac{2}{\pi}(1+\gamma)^{1/2}\frac{V_{\text{th}}}{V}\int_0^1 \left[\frac{(1+\kappa x^2)}{(1+\gamma x^2)}\right]^{1/2} \mathrm{d}x \tag{6}$$

where C_{R} may be called the reduced capacitance. $C_\parallel$ is the capacitance of the cell when the nematic is homeotropically oriented, i.e. the value of C in the limit $1/V \to 0$. $\varepsilon_\parallel$ and $\varepsilon_\perp$ may be obtained, respectively, by dividing $C_\parallel$ and $C_\perp$ by the empty cell capacitance C_0. In the above equation use has been made of the relation $\gamma = (C_\parallel - C_\perp)/C_\perp$.

Thus equation (5) predicts that a plot of $(C - C_\perp)/C_\perp$ against $1/V$ for $V \gg V_{\text{th}}$ should be linear, and the extrapolated value of the ordinate for $1/V \to 0$ should directly provide the value of $\gamma = \Delta\varepsilon/\varepsilon_\perp$. This procedure for obtaining γ was first suggested by Meyerhofer [7].

The variation of capacitance with applied voltage was fitted against equations (2) and (3) to obtain V_{th} and κ. We then used equation (1) to calculate K_{11} and hence K_{33}. This method for obtaining V_{th} and κ was suggested by Morris *et al.* [8].

The viscous behaviour of a nematic can be observed by studying the response to a sudden change of an applied magnetic or electric field which is normally stronger than the Fréedericksz threshold value. In case of deformations involving a pure twist there is no hydrodynamic flow. The molecules merely rotate without any translational motion and the analysis is rather simple [9]. In the case of a splay geometry, which is the case we have studied, the situation is far more complicated since the director orientation is now accompanied by a hydrodynamic flow. The gradient of the angular velocity of the director produces a backflow motion, first demonstrated by Pieranski *et al.* [10], giving rise to a frictional torque. The sudden removal of an external field in this case would result in a director relaxation time

$$\tau = \gamma_1^* d^2/(\pi^2 K_{11}) \tag{7}$$

where γ_1^* is the effective rotational viscosity coefficient, d is the cell thickness and K_{11} is the splay elastic constant. In practice γ_1^* is about 10% less than the rotational viscosity coefficient γ_1.

For the rotational viscosity coefficient measurements, we used a Hewlett-Packard impedance gain-phase analyser HP 4194A in the programmable mode, to record the decay of capacitance with time. An integration time of 500 µs was chosen which resulted in an interval of 5 ms between successive readings at the operating frequency which was fixed at 10 kHz. With this instrument a delay time, in multiples of 1 ms, could be introduced between the readings but in this case no delay was introduced since the capacitance decay was found to be quite fast. The a.c. probe voltage across the sample cell was held fixed at 0.3 V. A low frequency a.c. voltage of 2.0 V peak-to-peak was applied across the cell for about 30 s. The transient capacitance of the cell was captured as a function of time by switching off the low frequency a.c. voltage. A plot of this exponential decay of capacitance with time was then fed into a HP 7475A plotter connected to the impedance analyser over a HPIB bus. From the plots thus obtained for different concentration of biphenyl mixtures, at different temperatures, the time constant τ was calculated; using the values of K_{11} obtained from the static capacitance measurements, the effective rotational viscosity coefficient, γ_1^* was then evaluated.

3. Results and discussion

The transition temperatures T_{NI} (upper), (the lowest temperature at which the sample is isotropic) and T_{NI} (lower), (the highest temperature at which the sample is entirely nematic) were determined from optical texture studies and the results are presented in table 1 and figure 1. At T_{NI} (upper) the field of view of the polarizing microscope becomes completely dark. The width of the

Table 1. Variation of phase transition temperatures T_{NI} (°C) with concentration of biphenyl in 7CB.

Concentration/%	T_{NI} (lower)	T_{NI} (upper)
0.0	41.8	41.8
1.0	39.8	40.2
2.0	38.4	38.8
3.0	36.9	37.4
4.0	35.1	35.9
5.0	33.8	34.7
6.0	32.0	33.2
7.0	30.3	31.6
7.6	29.3	30.7
8.0	28.7	30.6

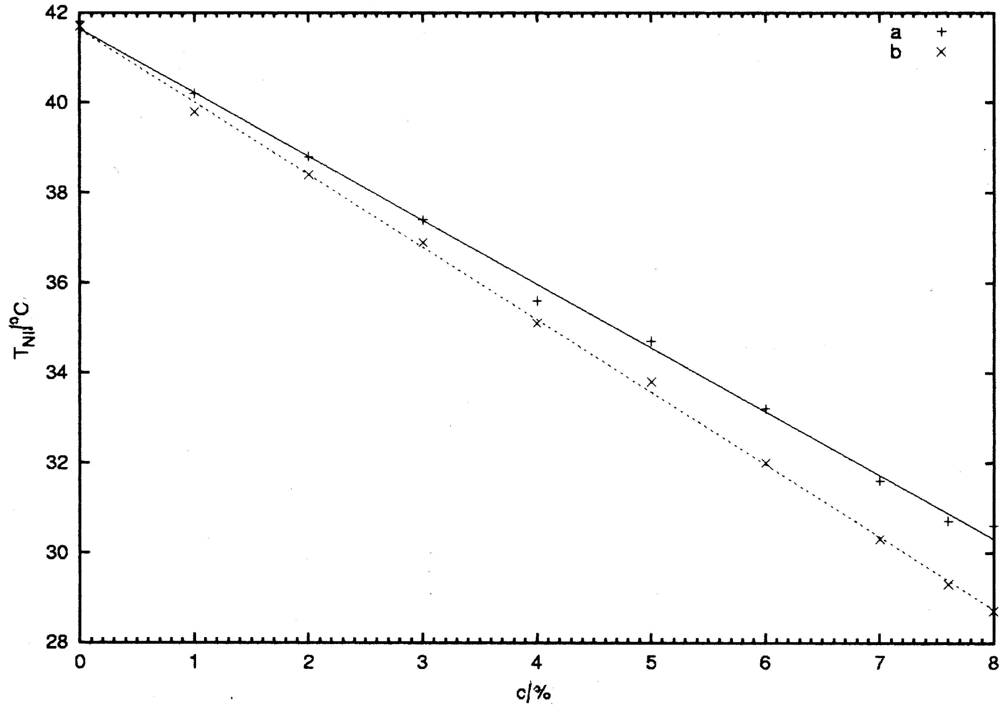

Figure 1. Variation of T_{NI} with concentration of biphenyl, c. a = T_{NI} (upper), b = T_{NI} (lower).

two-phase region was seen to increase with the concentration of biphenyl and for the maximum concentration of 8.0% this was 1.9 K.

Referring to the phase diagram as depicted in figure 1, incremental addition of solute at a fixed temperature T^* (where $T^* = T/T_{\mathrm{NI}}$) to an originally pure nematic material results in the initial appearance of the isotropic phase at x_{n} and final disappearance of the nematic phase at x_{i}. Defining $\gamma_{\mathrm{n}}^{\infty}$ and $\gamma_{\mathrm{i}}^{\infty}$ to be the infinite dilution activity coefficients at x_{n} and x_{i}, respectively, and $\beta_{\mathrm{n}}^{\infty}$ and $\beta_{\mathrm{i}}^{\infty}$ as, respectively, the limiting slopes of the nematic and isotropic boundary in the phase diagram, we have according to Martire [11]

$$\frac{\beta_{\mathrm{n}}^{\infty}}{\beta_{\mathrm{i}}^{\infty}} = \frac{x_{\mathrm{i}}}{x_{\mathrm{n}}} = \frac{\gamma_{\mathrm{n}}^{\infty}}{\gamma_{\mathrm{i}}^{\infty}} \tag{8}$$

and

$$\frac{1}{\beta_{\mathrm{n}}^{\infty}} - \frac{1}{\beta_{\mathrm{i}}^{\infty}} = \frac{\Delta S_{\mathrm{NI}}}{R}. \tag{9}$$

At a fixed temperature T^*

$$x_{\mathrm{i}} - x_{\mathrm{n}} = \frac{\Delta S_{\mathrm{NI}}}{R}(1 - T^*) \tag{10}$$

where ΔS_{NI} is the nematic–isotropic transition entropy for the pure nematic solvent.

Equation (10) shows that if $\Delta S_{\mathrm{NI}} \neq 0$ a two-phase region must exist at fixed T^* and that the size of this region depends only on the magnitude of ΔS_{NI}. From the phase diagram obtained by us experimentally the slopes $\beta_{\mathrm{n}}^{\infty}$ and $\beta_{\mathrm{i}}^{\infty}$ can be calculated. Using equation (9) the value of the N–I transition entropy ΔS_{NI} is found to be 0.822 $\mathrm{J^{-1}\,K^{-1}\,mol^{-1}}$.

The temperature dependence of $\varepsilon_{\|}$ and $\varepsilon_{\perp}$ for the concentration c of biphenyl ranging from 0 to 8.0% is shown in figure 2. An interesting behaviour was observed as the nematic–isotropic transition was approached. It was seen that with increase of concentration of biphenyl in the samples the value of $\varepsilon_{\|}$ approaches that of $\varepsilon_{\perp}$.

The temperature dependence of the dielectric anisotropy $\Delta\varepsilon$ is shown in figure 3. In the case of pure 7CB $\Delta\varepsilon$ was around 7.4 at T_{NI}, while it was seen to decrease as the amount of biphenyl in the mixtures increased, resulting in a $\Delta\varepsilon$ of about 0.5 in the 8.0% biphenyl mixture. However, this decrease in the value of $\Delta\varepsilon$ was seen to occur only within the two-phase region where the nematic and isotropic phases coexist. The value of $\Delta\varepsilon$ before the onset of the two-phase region in all the 7CB–biphenyl mixtures was more or less the same as that of pure 7CB at the N–I transition.

Another interesting feature was observed within the two-phase region. Here the variation of $\Delta\varepsilon$ with T was

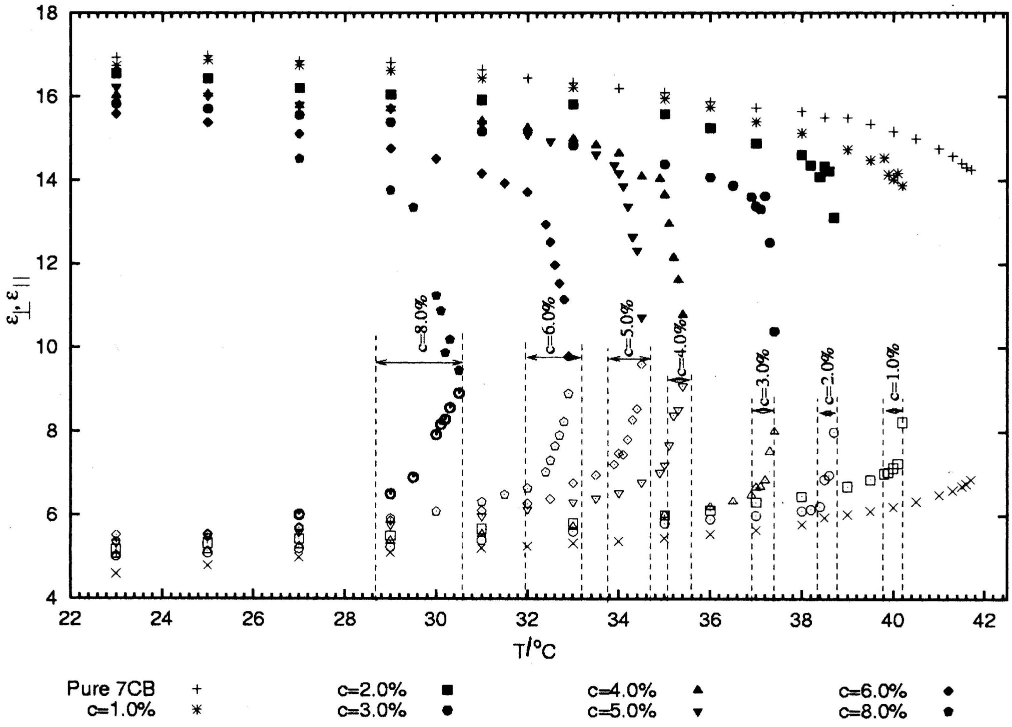

Figure 2. Variation of $\varepsilon_{\|}$ and $\varepsilon_{\perp}$ with T for different concentrations of biphenyl in 7CB. The vertical lines denote the transition temperatures T_{NI} (lower and upper) for different concentrations of biphenyl in 7CB as shown in table 1.

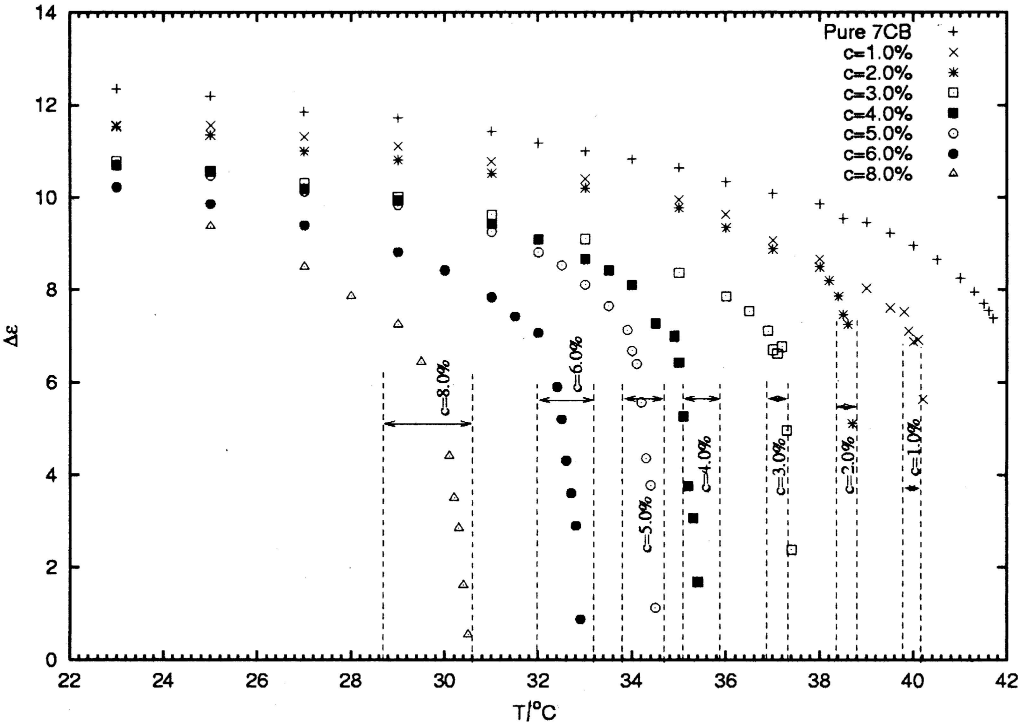

Figure 3. Variation of $\Delta\varepsilon$ with T for different concentrations of biphenyl in 7CB. The vertical lines denote the transition temperatures T_{NI} (lower and upper) for different concentrations of biphenyl in 7CB as shown in table 1.

seen to be linear with $\mathrm{d}(\Delta\varepsilon)/\mathrm{d}T$ having almost the same slope in all the 7CB–biphenyl mixtures as shown in table 2. It may be noted from this table that except for the lowest concentration of biphenyl (where the two-phase region is very narrow), the rate of change of $\Delta\varepsilon$ with respect to temperature is nearly constant and shows no systematic variation with concentration of biphenyl. One may be tempted to conclude that the decrease in the value of $\Delta\varepsilon$ within the two-phase region is because the percentage of isotropic patches which arises with the onset of transition within the coexistence region increases with increase in the concentration of biphenyl.

The temperature and concentration dependences of the splay elastic constant K_{11} are shown in figure 4. Here too, as in the case of $\Delta\varepsilon$, the variation within the two-phase region was seen to be approximately linear, (table 3). It is evident from this table that for biphenyl concentration of 3.0% onwards the slope $\mathrm{d}K_{11}/\mathrm{d}T$ decreases slightly, the plot of K_{11} vs T always remaining linear.

The temperature and concentration dependence of the bend elastic constant is shown in figure 5. The temperature dependence of the rotational viscosity coefficient for 0 to 8.0% biphenyl concentration is shown in figure 6. Here an interesting observation was made. For impurity concentrations of 4.0% and above, γ_1^* shows a sharp increase as the nematic–isotropic transition temperature is approached. This is manifested in a huge increase in the time constant of the capacitance decay as the transition is approached.

Table 2. $\mathrm{d}(\Delta\varepsilon)/\mathrm{d}T$ for different concentrations of biphenyl in 7CB.

Concentration/%	$\mathrm{d}(\Delta\varepsilon)/\mathrm{d}T$
1.0	−4.69
2.0	−8.46
3.0	−8.18
4.0	−10.35
5.0	−9.23
6.0	−9.33
8.0	−9.63

Table 3. $\mathrm{d}K_{11}/\mathrm{d}T$ for different concentrations of biphenyl in 7CB.

Concentration/%	$\mathrm{d}K_{11}/\mathrm{d}T$
1.0	−1.80
2.0	−1.36
3.0	−3.44
4.0	−3.15
5.0	−3.07
6.0	−2.90
8.0	−2.60

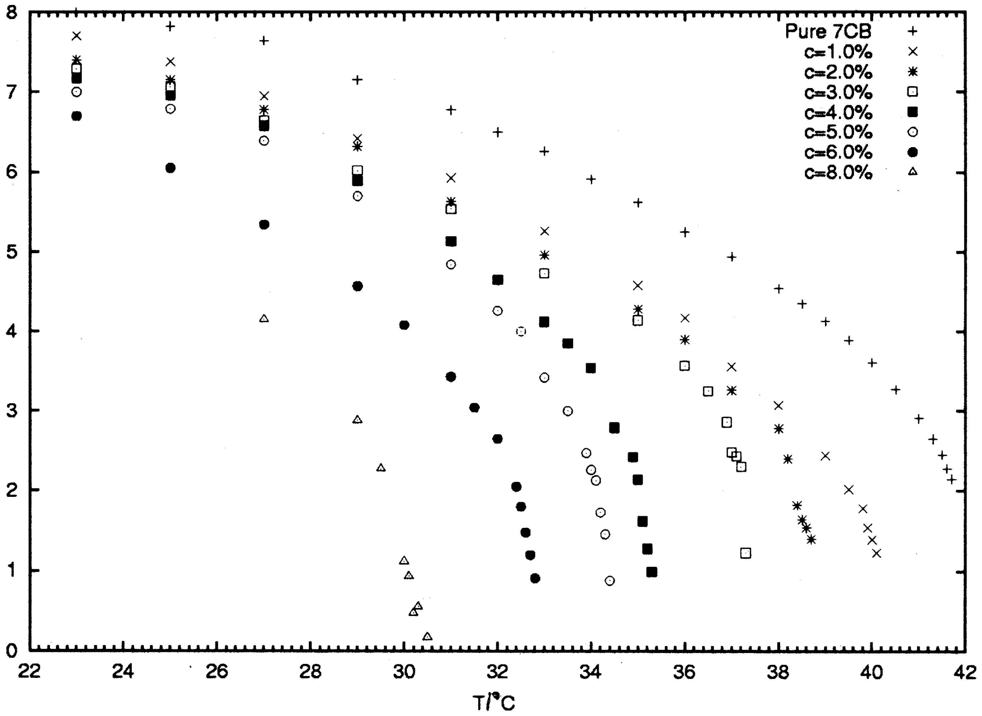

Figure 4. Variation of K_{11} with T for different concentrations of biphenyl in 7CB.

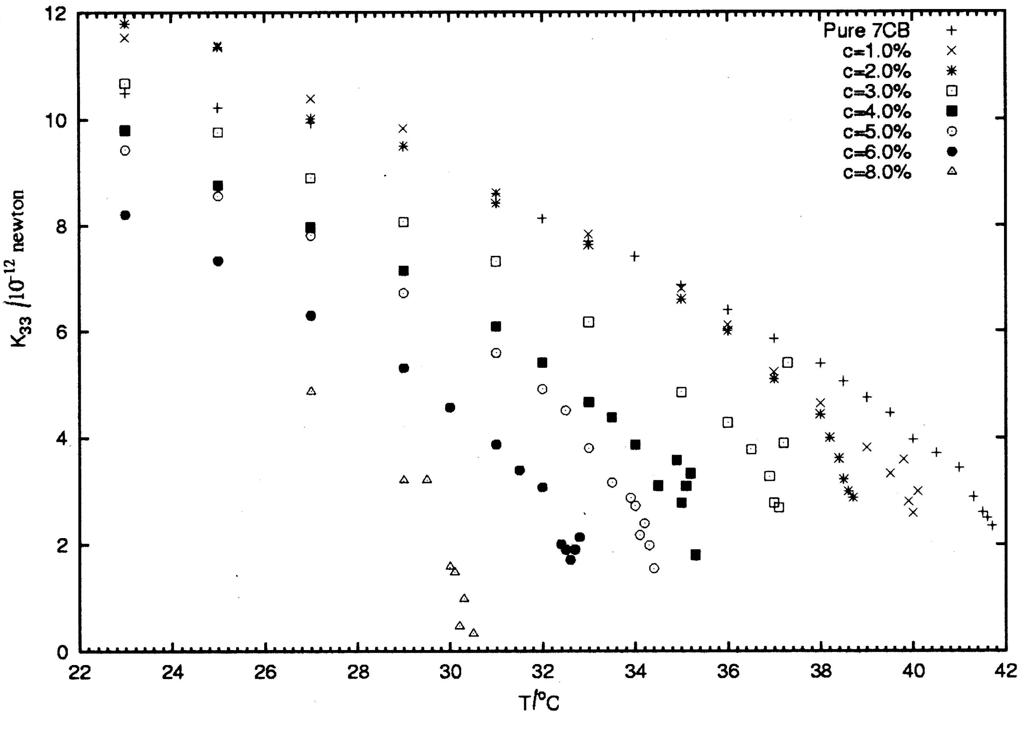

Figure 5. Variation of K_{33} with T for different concentrations of biphenyl in 7CB.

4. Conclusions

It is clear that the presence of the non-mesogenic solute biphenyl reduces the degree of nematic ordering in 7CB. This is possibly because of the diluting effect of biphenyl on the anisotropic interactions between the 7CB molecules which give rise to the nematic phase. The estimation of the entropy of transition ΔS_{NI} of 7CB from the slopes of the transition temperatures gives a

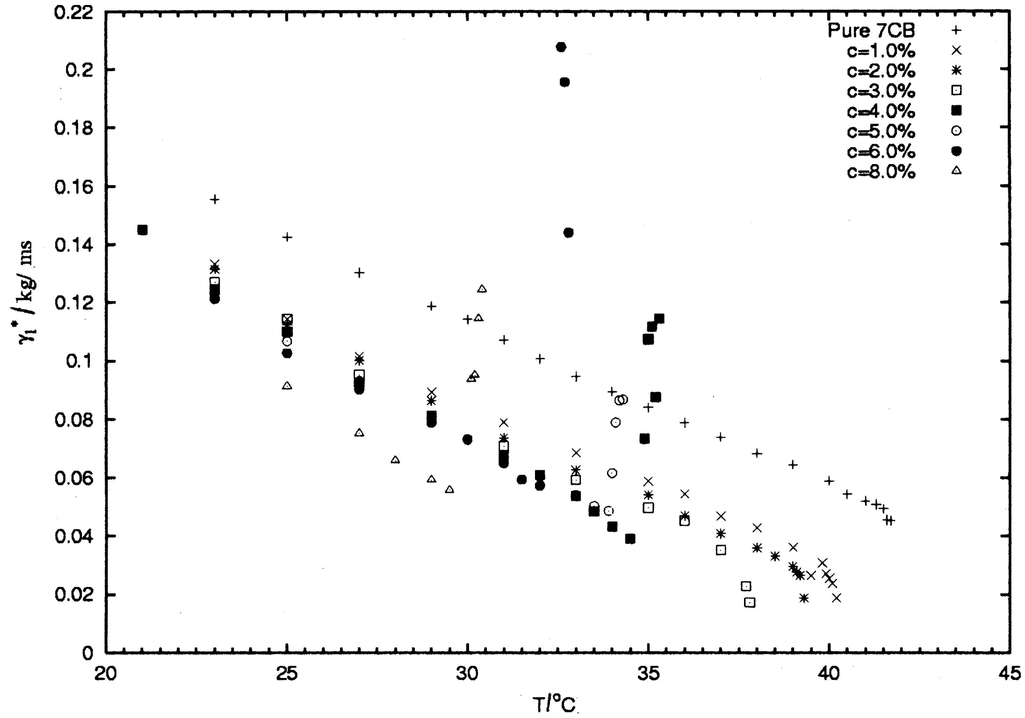

Figure 6. Variation of γ_1^* with T for different concentrations of biphenyl in 7CB.

value which compares well with the prediction of the Maier–Saupe theory. As the temperature was increased beyond T_{NI} (lower) we could see the appearance of isotropic patches when the sample was observed under the polarizing microscope. It was clearly seen that the proportion of the isotropic part increased with temperature thus explaining the rapid fall of $\Delta\varepsilon$ and K_{11}. A notable feature is that within the mixed phase the fall of these quantities was found to be very nearly linear, with slopes which were independent of the concentration of biphenyl for $\Delta\varepsilon$, and decreasing slowly with c for K_{11}.

It would have been interesting if one could measure the proportions of the volumes of the two co-existing phases, nematic and isotropic, in the two phase region and correlate this with the decrease in $\Delta\varepsilon$ with temperature. The ratio of volumes of the nematic and isotropic parts really translates into the ratio of the areas of the two types of patches in a thin cell, but it is a difficult task to measure the areas under a polarizing microscope because of their completely irregular shape.

We also point out that along T_{NI} (lower) where the isotropic phase begins to appear, the dielectric anisotropy $\Delta\varepsilon$ was found to be nearly constant. If one assumes that $\Delta\varepsilon$ is approximately proportional to the long range nematic order parameter, then this is an interesting observation. As regards the rotational viscosity coefficient, this exhibits a sharp increase in the neighbourhood of the nematic–isotropic transition for the higher concentrations of biphenyl. Any attempt to explain theoretically the behaviour of the mixed phase should take account of these features.

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