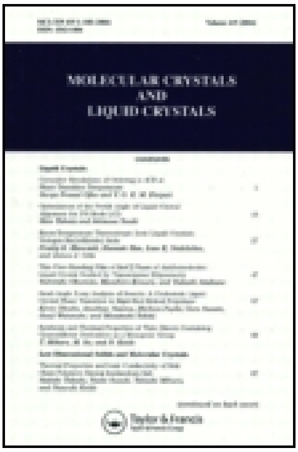

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Determination of K33/K11 Ratio of a Polar-Nonpolar Mixture Showing Injected Smectic Phase

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DETERMINATION OF K33/K11 RATIO OF A POLAR-NONPOLAR MIXTURE SHOWING INJECTED SMECTIC PHASE.

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Abstract The ratio of the bend to splay elastic constant of a binary liquid crystalline mixture (5CB/ME6O.5) which show injected smectic phase, has been determined by Freedericksz transition in nematic phase, results of which have been reported here. It has been found that K_3/K_1 values show a divergence as the injected smectic phase is approached. The K_3/K_1 values also show a minimum near equimolar concentration, which is similar to the minimum in other physical properties of this mixture at this concentration found by previous workers.

INTRODUCTION

Measurements of Frank elastic constants play an important role in characterising liquid crystal display devices. Especially, the ratio of the bend to splay elastic constants K_3/K_1 is one of the controlling parameters affecting the sharpness of electro - optic response of display devices. Since, generally, no pure compound has the required nematic range, mixtures of mesomorphic compounds are used in nematic displays. One of the unusual aspects of binary liquid crystal mixtures of strongly dipolar and weakly dipolar mesogens is the formation of smectic phases, called injected smectic phases, from components which do not show smectic properties in their pure state [1–4]. Though the formation of injected smectic phase is undesirable in liquid crystal display (LCD) materials, its presence at a lower temperature than the working temperature of the LCD may be helpful under certain conditions[5]. With this view in mind we have measured the bend to splay elastic constant (K_3/K_1) ratios of a binary liquid crystalline mixture comprising of 4-n-pentyl -4'-cyanobiphenyl (5CB) and 4-n- pentyl phenyl - 4-n'- hexyloxy benzoate (ME6O.5) at different compositions. This mixture shows the presence of an injected smectic phase, some of the physical properties of which have been studied earlier in our laboratory by Das *et al* [6–8]. They have measured the refractive indices and density [6], as well as calculated orientation order parameters [7] and layer thickness[8] from x-ray diffraction studies [7,8] at different compositions of this mixture over their mesomorphic range.

One of the most convenient methods of determining elastic constants is from Freedericksz transition, where an electric or magnetic field is applied to deform a thin layer of surface aligned nematogenic sample. Depending on the geometry of the arrangement, splay, twist or bend elastic constant can be determined from Freedericksz transition [9]. Measurements of the bend to splay elastic constant ratios have been carried out at different compositions of this mixture in their nematic phase only. Temperature dependence of (K_3/K_1) values for different compositions of the mixtures have been studied. The splay and bend elastic constants of n- pentyl cyanobiphenyl (5CB) have been widely reported by several authors [10-13]. In this paper we have taken the (K_3/K_1) values of 5CB reported from our laboratory [13] by Das *et al.* Since no magnetic susceptibility anisotropy data on these mixtures have been reported so far it has not been possible to determine the individual values of the bend (K_3) and splay (K_1) elastic constants.

EXPERIMENTAL

The phase diagram of this system has already been given by Das and Paul and the nematic-isotropic and induced smectic A-nematic phase transition temperatures for different concentrations of this mixture, as obtained from this phase diagram, are listed in Table I.

TABLE I Mole fraction and transition temperatures of different mixtures.

Name of the mixtures	Mole fraction of 5CB (x)	Induced SmA - N transition temp. T_{AN}(°C)	N - Iso. transition temp. T_{NI}(°C)
H	0.1504	37.8	50.6
D	0.4017	53.3	56.7
C	0.5001	56.7	59.0
A	0.6455	—	47.1
F	0.7316	49.5	61.6

The experimental set up for the determination of elastic constants have been described in detail in our earlier publication[13]. The liquid crystal samples were filled in a specially surface treated glass cell of thickness of about 50 μm. A polarized light beam from sodium vapour lamp was passed through the cell and a crossed analyser was placed before a photomultiplier tube (RAC 931) used for measuring the transmitted light intensity. The current output from the photomultiplier tube was amplified and measured. The output current from the photomultiplier was calibrated for relative light intensity using two plane polarisers with different angles between their plane of polarisation. The magnetic field was measured with the help of a calibration hall probe. The critical magnetic field for the Freedericksz transition could be observed from the sudden change in the current from the photomultiplier tube. The relevant elastic constant $K_i (i = 1,3)$ was calculated using the equation

$$K_i = H_c^2 d^2 \Delta\chi / \pi^2$$

where H_c is the critical field with geometry relevant for the particular elastic constant measurement, d the thickness of the sample and $\Delta\chi$ the magnetic susceptibility anisotropy. However, since no magnetic susceptibility data is available for this mixture, the value of the ratio K_3/K_1 is only given in this paper.

RESULTS AND DISCUSSION

The bend to splay elastic constant ratios (K_3/K_1) for different compositions of the binary mixture (ME6O.5 + 5CB) were measured by us in the nematic phase only, since the bend elastic constant tends to infinity in smectic liquid crystals. The results are plotted in Figures 1 and 2. As mentioned in the introduction, the bend and splay elastic constants and their ratio (K_3/K_1) for 5CB have been reported earlier[13] from our laboratory. From Figure 1 it is seen that in the region of the phase diagram where the mixtures show injected smectic phase, (i.e. Mixture A(mole fraction of 5CB, x= 0.6455), Mixture C(x= 0.5001), Mixture D(x= 0.4017) and Mixture H(x=0.1504)) there is a sharp increase in the K_3/K_1 values particularly near the smectic A - nematic transition temperatures. This divergence of the bend to splay ratios has also been reported by Bradshaw *et al* in hybrid mixtures containing phenyl benzoate esters . Possible reason for this may be formation of smectic clusters as pre-transitional effect. Since for smectics K_3/K_1 is almost infinity, the presence of these smectic clusters enhances the value of K_3/K_1. In mixture F(x= 0.7316), however, such rapid increase in K_3/K_1 values is not found, possibly because this mixture was studied in the temperature range which is far away from the injected smectic phase region. The K_3/K_1 values of ME6O.5 are found to be higher than that of 5CB. Temperature variation of K_3/K_1 ratio for ME6O.5 is also found to be greater than that for 5CB.

In Figure 2, we have plotted the K_3/K_1 values at $(T_{NI}\text{-}2)^\circ$ C against mole fraction of 5CB. It is clear from the figure that K_3/K_1 values, near the clearing temperature, show a minimum near equimolar concentration. Previous workers[6–8]

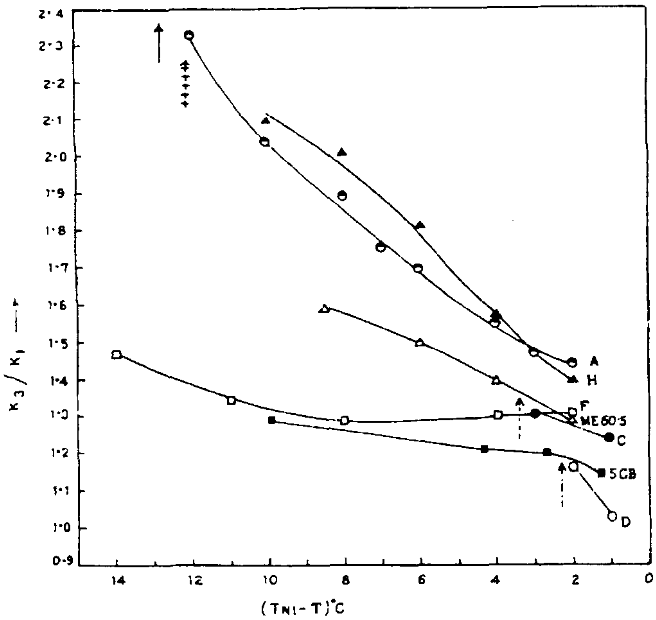

FIGURE 1 Ratio of the bend to splay elastic constants K_3/K_1 as function of relative temperature $(T_{NI} - T)^0C$ for the different mixtures and the pure compounds. Key to symbols : ⊖, mixture A, ↑ indicates smectic A - nematic transition temperature (T_{AN}) for mixture A; ●, mixture C, ↑ indicates T_{AN} for mixture C; o, mixture D, ↑ indicates T_{AN} for mixture D; □, mixture F; ▲, mixture H, ↑ indicates T_{AN} for mixture H; △, ME6O.5; ■, 5CB[13]. Lines drawn are guide to the eye only.

have also observed a similar trend in the variation of birefringence[6], density[6], orientational order parameters <P_2> and <P_4>[7] and layer thickness[8] of this mixture. Similar behaviour have also been reported by Dunmur *et al* in a related mixture (ME5O.5 + 5CB)[4]. Further analysis of the elastic constants data is not possible due to the absence of magnetic susceptibility data for the mixture (ME6O.5 + 5CB) reported in this paper. Magnetic susceptibility measurements on this mixtures will help in providing better physical understanding of this system.

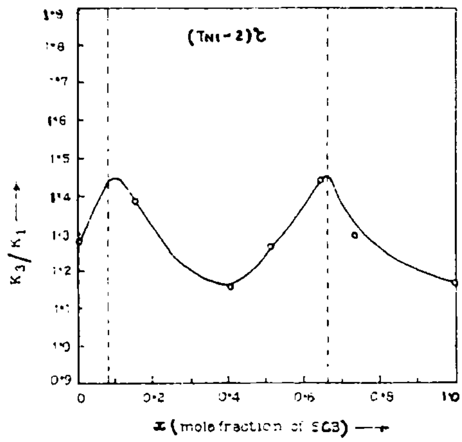

FIGURE 2 The bend to splay elastic constant ratios plotted against mole fraction of 5CB at a fixed relative temperature $(T_{NI} - 2)^0C$. Line drawn is guide to the eye only. The dotted vertical lines indicate the extent of the injected smectic phase. x is the mole fraction of 5CB.

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