

CHAPTER - 8

***DETERMINATION OF ELASTIC CONSTANTS OF A POLAR - NONPOLAR
MIXTURE SHOWING INJECTED SMECTIC PHASE***

8.1 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 I 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 (ME60.5) 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.

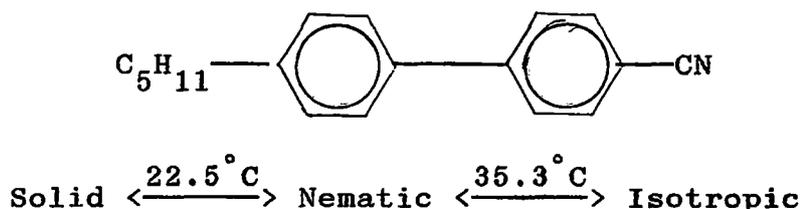
One of the most convenient methods of determining elastic constants is from Freedericksz transition, where an electric or magnetic field is applied to deform a thin layer of surface

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 has been studied. The splay and bend elastic constants of n-pentyl cyanobiphenyl (5CB) have been widely reported by several authors [10-13]. In this chapter I 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.

8.2 Experimental

The liquid crystal samples were donated by E. Merck, U.K. and were used without further purification. The chemical names, molecular structure and transition temperatures of the two components are given below:

Component 1: 4-n-pentyl -4' - cyanobiphenyl (5CB)



Component 2: 4-n-pentyl phenyl - 4-n' - hexyloxy benzoate (ME60.5)

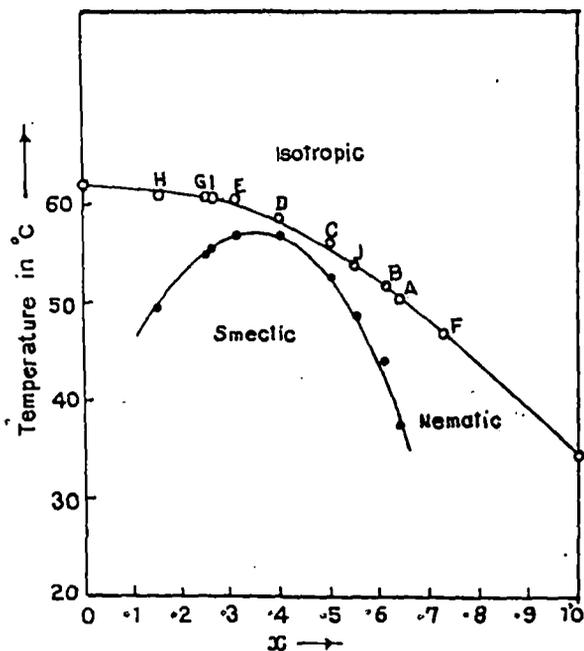
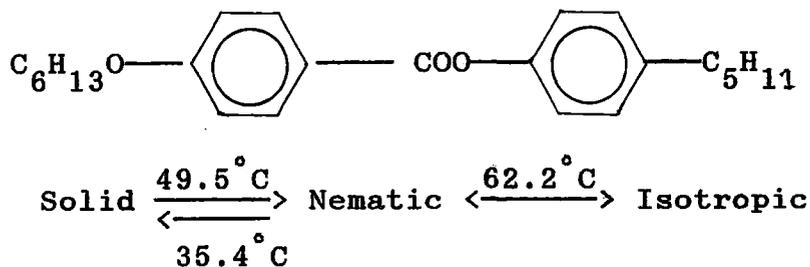


Figure 8.1 Temperature—concentration phase diagram for the binary system of 4-*n*-pentyl-4'-cyanobiphenyl (5CB) and 4-*n*-pentyl phenyl-4-*n*'-hexyloxy benzoate (ME60.5). x is the mole fraction of 5CB. \circ nematic-isotropic transition temperature. \bullet smectic-nematic transition temperature (reference 6).



The phase diagram of this system as obtained by Das and Paul [6] is shown in Figure 8.1. The nematic-isotropic and induced smectic A-nematic phase transition temperatures are plotted against mole fraction of 5CB (x) in Figure 8.1 and the corresponding transition temperatures of different compositions of this mixture are shown in table 8.1. Mixtures for the same concentration (as given in Figure 8.1) were prepared by me, by weighing materials into a small glass bottle and mixing thoroughly by agitating the heated mixture in its isotropic state and keeping at that temperature for about twenty four hours to ensure the formation of a homogeneous mixture. The transition temperatures of the mixtures thus prepared were checked under a polarising microscope equipped with a Mettler FP-80/82 Thermo system, and were found to agree with the literature values [6].

The experimental set up for the determination of elastic constants has been described in chapter 2. The liquid crystal samples were filled in a specially surface treated glass cell of thickness of about $50\mu\text{m}$. Depending upon the surface treatment, either planar or homeotropic alignment were produced. The cells were examined under a polarising microscope to check the uniformity of alignment before using in the experiment. The cells were placed in a brass thermostat with glass windows. The temperature of the thermostat was kept constant within $\pm 0.5^\circ\text{C}$ during the experiment using a temperature controller (Indotherm-457). The sample cell with the thermostat was placed in a magnetic field with relevant

geometry [7] for the measurement of splay or bend elastic constant. 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 magnetic field was measured with the help of a calibration hall probe. The critical magnetic field for the Fredericksz transition could be observed quite accurately (within 0.5%) from the sudden change in the current from the photomultiplier tube. The relevant elastic constant K_i ($i = 1,3$) was calculated from the well known 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 thesis.

8.3 Results and Discussions

The bend to splay elastic constant ratios (K_3/K_1) for different compositions of the binary mixture (ME60.5 + 5CB) was measured by me in the nematic phase only, since the bend elastic constant tends to infinity in smectic liquid crystals. The results are plotted in Figures 8.2 and 8.3. 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 8.2 it is seen that in the

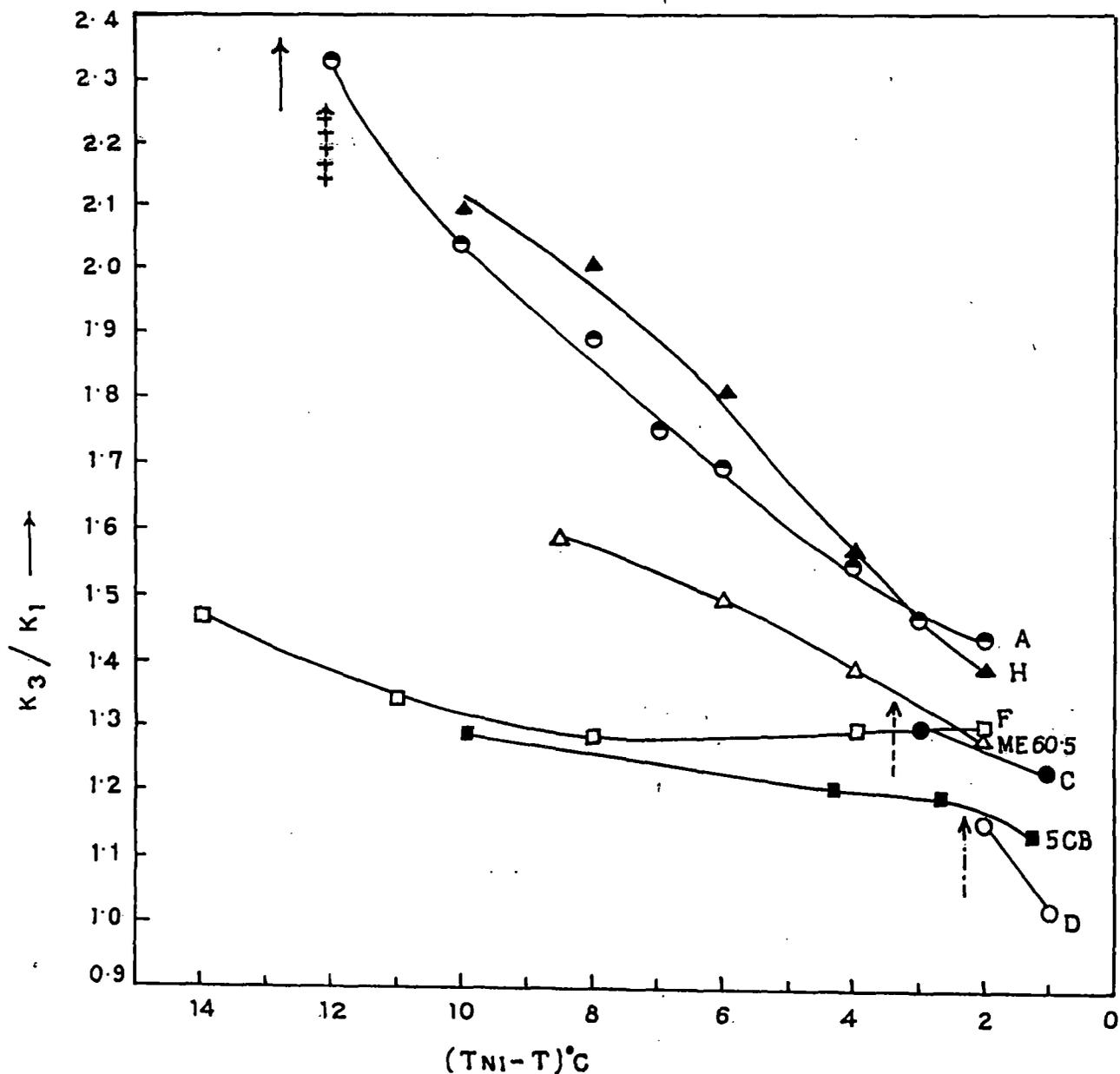


Figure 8.2 Ratio of the bend to splay elastic constants K_3/K_1 as function of relative temperature $(T_{NI} - T)^\circ\text{C}$ for the different mixtures and the pure compounds. Key to symbols : ●, mixture A, ↑ indicates smectic A - nematic transition temperature (T_{AN}) for mixture A; ●, mixture C, ↑ indicates T_{AN} for mixture C; ○, mixture D, ↑ indicates T_{AN} for mixture D; □, mixture F; ▲, mixture H, ↑ indicates T_{AN} for mixture H; △, ME60.5; ■ 5CB [13]. Lines drawn are guide to the eye only.

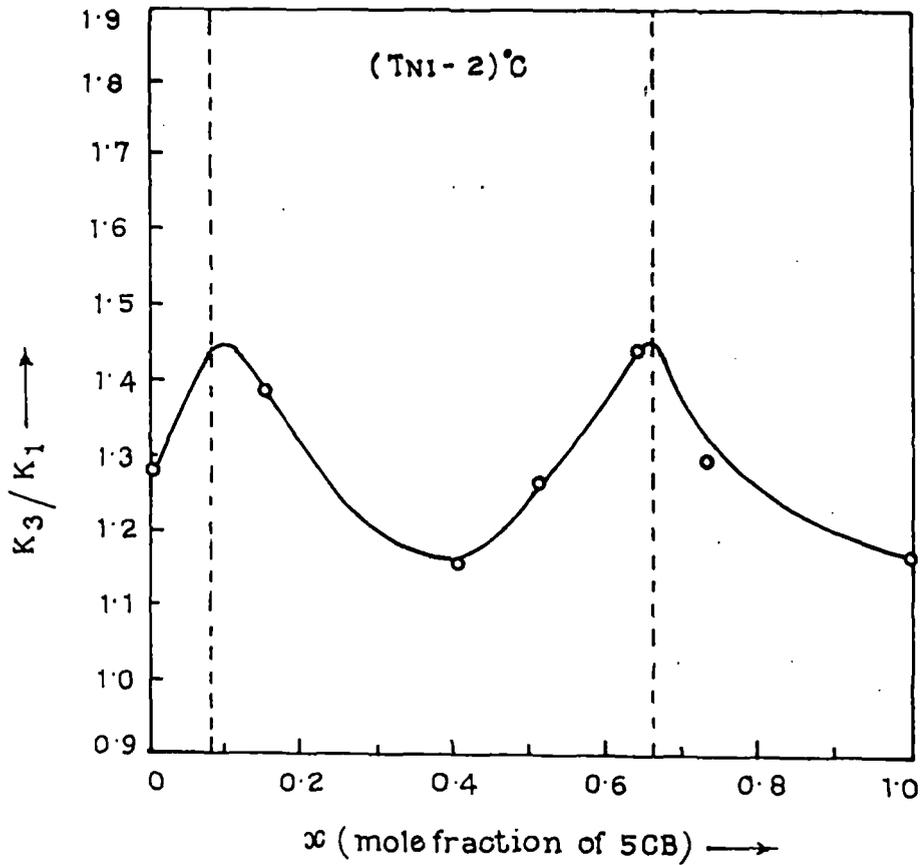


Figure 8.3 The bend to splay elastic constant ratios plotted against mole fraction of 5CB at a fixed relative temperature $(T_{NI} - 2)^\circ\text{C}$. Lines drawn are guide to the eye only. The dotted vertical lines indicate the extent of the injected smectic phase. x is the mole fraction of 5CB.

region of the phase diagram (Figure 8.1) where the mixtures show injected smectic phase, (Mixtures A,C,D and H) 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 [14]. 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, 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 ME60.5 are higher than that of 5CB. Temperature variation of K_3/K_1 ratio for ME60.5 is also greater than that for 5CB. The Frank elastic constant ratio's for different composition of this mixture, together with those of the pure compounds is included in table 8.2.

In Figure 8.3, I have plotted the K_3/K_1 values at $(T_{NI}-2)^{\circ}\text{C}$ 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] have also observed a similar trend in the variation of birefringence [6], density [6], orientational order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ [7] and layer thickness [8] of this mixture. Similar behaviour have also been reported by Dunmur et al in a related mixture (ME50.5 + 5CB) [4]. Further analysis of the elastic constants data is not possible due to the absence of magnetic susceptibility data for the mixture (ME60.5 + 5CB) reported in this thesis. Magnetic susceptibility measurements on this mixtures are currently being done in our laboratory which will help in providing better physical understanding of this system.

Table 8.1

Mole fraction and transition temperatures of different mixtures [6].

Name of the mixtures	Mole fraction of 5CB	T _{AN} (°C)	T _{NI} (°C)
A	0.6455	37.8	50.6
C	0.5001	53.3	56.7
D	0.4017	56.7	59.0
F	0.7316	—	47.1
H	0.1504	49.5	61.6

Table 8.2

Sample : ME60.5, 5CB and mixture F.

Temperature dependence of Frank elastic constant ratio's K_3/K_1 .

ME60.5		5CB*		mixture F	
$(T_{NI}-T)^{\circ}C$	K_3/K_1	$(T_{NI}-T)^{\circ}C$	K_3/K_1	$(T_{NI}-T)^{\circ}C$	K_3/K_1
2.0	1.28	1.3	1.14	2.0	1.31
4.0	1.39	2.7	1.20	4.0	1.30
6.0	1.50	4.3	1.21	8.0	1.28
8.5	1.59	10.0	1.29	11.0	1.33
				14.0	1.47

(continued)

* K_3/K_1 values taken from reference [13].

Table 8.2

Sample : mixture A, mixture C, mixture D and mixture H.

Temperature dependence of Frank elastic constant ratio's K_3/K_1 .

mixture A		mixture C		mixture D		mixture H	
$(T_{NI} - T)^\circ C$	K_3/K_1						
2.0	1.44	1.0	1.24	1.0	1.03	2.0	1.39
3.0	1.48	3.0	1.31	2.0	1.16	4.0	1.58
4.0	1.56					6.0	1.81
6.0	1.70					8.0	2.01
7.0	1.75					10.0	2.09
8.0	1.89						
10.0	2.04						
12.0	2.34						

REFERENCES

- [1]. J. S. Dave, P. R. Patel and K.L.Vasant, Mol. Cryst. Liq.Cryst., 8, 93 (1969).
- [2]. B. Engelen and F. Schneider, Z. Naturforsch.,33a, 1077 (1978).
- [3]. C.S. Oh Mol. Cryst. Liq. Cryst., 42, 1 (1977).
- [4]. D.A. Dunmur, R.G. Walker and P. Palffy-Muhoray, Mol.Cryst. Liq. Cryst. 122, 321 (1985)
- [5]. N. V. Madhusudana, Liquid Crystals, Applications and uses, (Ed. B. Bahadur), World Scientific, Vol. 1, 1991.
- [6]. M.K. Das and R. Paul, Phase Transitions, 46, 185 (1994).
- [7]. M.K. Das and R. Paul, Phase Transitions, 48, 255 (1994).
- [8]. M. K. Das and R. Paul, Mol. Cryst. Liq. Cryst., 260, 477 (1995)
- [9]. W.H. de Jeu, Physical Properties of Liquid Crystalline Materials, Chapter 6, Gordon and Breach Science Publisher, New York, 1980.
- [10]. P. Karat and N. V. Madhusudana, Mol. Cryst. Liq. Cryst., 40, 239 (1977).
- [11]. H. Hakemi, E. F. Jagodzinski and D. B. Dupre, J. Chem. Phys., 78, 1513 (1983).
- [12]. M. Hara, J. Hirakata, T. Tayooka, H. Takazoe and A. Fukuda, Mol. Cryst. Liq. Cryst., 122, 161 (1985).
- [13]. M. K. Das and R. Paul, Mol. Cryst. Liq. Cryst. (in press).
- [14]. M.J. Bradshaw and E.P. Raynes, Mol. Cryst. Liq. Cryst. 138, 307 (1986).