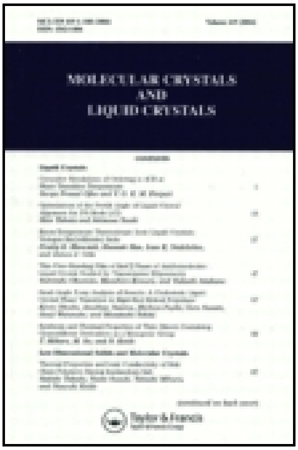

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

The Magnetic-Field-Induced Birefringence of the Mixtures of the Chiral Molecules and the Ferronematic Liquid Crystals

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To cite this article: Shu-Hsia Chen & S. H. Chiang (1987): The Magnetic-Field-Induced Birefringence of the Mixtures of the Chiral Molecules and the Ferronematic Liquid Crystals, Molecular Crystals and Liquid Crystals, 144:5, 359-370

To link to this article: http://dx.doi.org/10.1080/15421408708084229

Mol. Cryst. Liq. Cryst., 1987, Vol. 144, pp. 359–370
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Printed in the United States of America

The Magnetic-Field-Induced Birefringence of the Mixtures of the Chiral Molecules and the Ferronematic Liquid Crystals†

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The ferronematic state which was described theoretically by Brochard and de Gennes can be achieved by doping the liquid crystal with anisotropic ferromagnetic particles. The homeotropic liquid crystal film was successfully prepared for the ferronematic liquid crystal doped with low concentration chiral molecule.

The magnetic-field-induced-birefringence due to molecular reorientation was treated both theoretically and experimentally. In the low field regime (<2.5G), it is theoretically predicted that the induced phase difference between the ordinary and extraordinary ray of a normally incident probe beam is proportional to the square of the external magnetic field and to the fifth power of the thickness of the sample film. This is verified by the experimental results.

The effect of the chiral molecules appears in the effective elastic constant, k_e, which will decrease and then increase with respect to the increasing of the concentration of the chiral molecules.

Keywords: ferronematic, magnetic, birefringence, mixture, chiral molecules

INTRODUCTION

To influence the alignment of a nematic liquid crystal with magnetic fields, high-field intensities ($\geq 10^3$G) are required in order to overcome its typical minute anisotropy of the diamagnetic susceptibility ($X_a \simeq 10^{-7}$ cgs units). Brochard and de Gennes[1] constructed a theory of magnetic suspension in liquid crystals and they predicted that the coupling between the needle like magnetic grains and the liquid crys-

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†This work was supported partially by the Chinese National Council under contract no. NSC-75-0208-M009-01.

tal molecules, which is mechanical in nature, would result in a matrix with ferromagnetic behavior $[M(H = 0) = 0]$, which they call ferronematics or ferrocholesterics. They also predicted that, at a critical concentration of well dispersed magnetic particles, the matrix should exhibit collective orientational distortion with an instability threshold occurring at a critical field value. The observation of this macroscopic collective behavior of the ferronematics was reported by Chen and Amer.[2] The preparation of a well aligned ferrocholesterics is much more difficult. A mixture of the chiral molecules and ferronematics was prepared. This mixture can have helical structure with $PC =$ constant ($= 0.12$ μm in Ref. 3) where P is the natural pitch of the helix and C is the weight concentration of the chiral molecules.[4] Hass[5] reported that when $P/D > 3$, where D is the sample film thickness, this mixture can be aligned homeotropically.

In this paper, we report evidence of the collective behavior of a mixture of chiral molecules and ferronematics. The continuum theory was used in the theoretical calculation for the homeotropic cell. The Ho's[6] high-resolution birefringence measurement method was used in measuring the magnetic-field-induced molecular reorientation. The experimental results is compared with the theoretical prediction in the low field regime (<2.5G). The effect of the chiral molecules which appears in the effective elastic constant, K_e, is discussed.

THEORY

Consider a homeotropically aligned film of the mixture of chiral molecules and the ferronematic liquid crystal in an external magnetic field H. The magnetic grain is coupled to the nematic matrix such that the local magnetization $\vec{M}$ of the sample is perpendicular to the local nematic director $\hat{n}$.[2] The geometry is depicted in Figure 1. To find the magnetic-field-induced birefringence of the film, we must know the local average orientation of the molecules $\hat{n}$. This can be obtained by minimizing the total free energy F_T of this system, $F_T = \int F_d\, dV$, where the free-energy density F_d, which includes elastic, magnetic and entropy terms, takes the form

$$F_d = \frac{1}{2}[k_{11}(\vec{\nabla}\cdot\hat{n})^2 + k_{22}(\hat{n}\cdot\vec{\nabla}\times\hat{n})^2 + k_{33}(\hat{n}\times\vec{\nabla}\times\hat{n})^2]$$

$$- f\vec{M}_s\cdot\vec{H} - \frac{1}{2}\chi_a(\hat{n}\cdot\vec{H})^2 + \frac{fk_BT}{V}\ln f \quad (1)$$

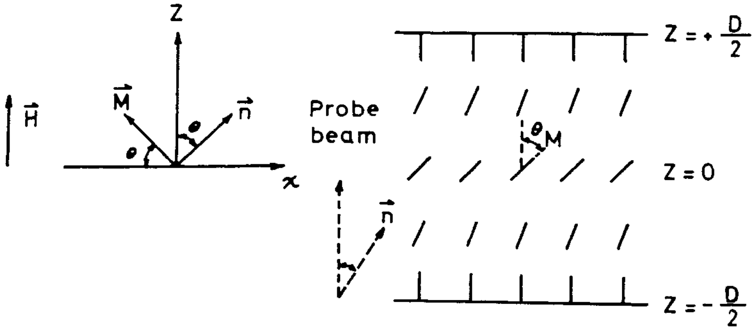


FIGURE 1 The molecular geometry.

where k_{11}, k_{22} and k_{33} are the splay, twist and bend elastic constants, respectively; k_B is the Boltzmann constant; M_s is the saturation magnetization of the magnetic grain; f is the filling factor that is the volume fraction of the magnetic grains; V is the volume of the sample and H is the strength of the externally applied magnetic field. Comparing to the contribution of the magnetic particles, the magnetic term of the liquid crystal was neglected for the small χ_a. For $\vec{H} = H\hat{z}$, assume $\vec{M}$ and $\hat{n}$ lying in the x-z plane and being a function of z only. If $\vartheta(z)$ is the angle between $\hat{n}$ and $\hat{z}$ at z, then $\hat{n} = \sin\vartheta(z)\,\hat{x} + \cos\,(z)\hat{z}$ and $\vec{M} = -M\cos\vartheta(z)\hat{x} + M\sin\vartheta(z)\hat{z}$. For small molecular orientational distortion ($\vartheta_M << 1$), the free energy per unit area of this system can be written in the following form:[2]

$$F = \int_{-D/2}^{D/2} dz \left\{ \frac{1}{2} k_{33}(1 + K \sin^2\theta) \left(\frac{d\theta}{dz}\right)^2 - MH\sin\theta \right\} \qquad (2)$$

where $M = M_s f$, $k = (k_{11} - k_{33})/k_{33}$ and D is the thickness of the sample.

By minimizing the free energy using the Euler-Lagrange equation, one can readily show that

$$\frac{d^2\theta}{dz^2} + \xi^{-2} = 0$$

where $\xi = [k_{33}/MH]^{1/2}$

When we take the boundary conditions $\vartheta(z = \pm D/2) = 0$, then

$$\theta(z) = \frac{1}{2}\xi^{-2}[(D/2)^2 - z^2] \qquad (3)$$

and

$$\theta_M = \theta(z = 0) = (MH/8k_{33})D^2 \tag{4}$$

The magnetic-field-induced molecular reorientation can be found by measuring the corresponding induced change in birefringence. For small distortion $\vartheta_M << 1$, it can be shown that the change in phase difference δ is given by[7]

$$\delta = \frac{2\pi}{\lambda}\left[\frac{8}{15} D^5(n_e - n_o)(M/8\ k_{33})^2\right]H^2 \tag{5}$$

where n_e and n_o are the extraordinary and ordinary indices of refraction of the liquid crystal, respectively, and λ is the wavelength of the light used to measure the birefringence change.

EXPERIMENTAL METHOD

The magnetic particles were γ-Fe_2O_3 needles 0.5 μm long and had an aspect ratio of 7:1, with a density of 4.78 g/cm^3 and saturation magnetization of 338.4 erg/G-cm^3. Their magnetic dipole moments pointed along the long axes of the particles. These needles were coated with dimethyl octadecyl aminopropyl trimethoxysilyl chloride (DMOAP) as prepared in previous work to prevent clumping. The nematic liquid crystal and chiral molecules used for this work were methoxybezyldene butylaniline (MBBA) and cholesteryl nonanoate (CN), respectively. The samples of various CN concentrations were achieved by mixing the mixtures of CN and MBBA and the suspension of γ-Fe_2O_3 in MBBA. The filling factor f was 5.67×10^{-5}.

The homeotropic alignment was obtained by coating slide glass substrates with DMOAP.[8] The sample was sandwiched between two slide glass with a mylar spacer. The thickness of the sample film was determined by focusing the microscope on the two interior surfaces of the glass. The sample film was inspected very carefully by crossed polarized microscope and conoscopy before the optical measurements.

The birefringence measurement setup is shown in Figure 2. Polarized light at wavelength $\lambda = 633$ nm from a He-Ne laser was divided into two beams with a beam splitter. The main beam passed successively through the sample, a quarter-wave plate and a rotating po-

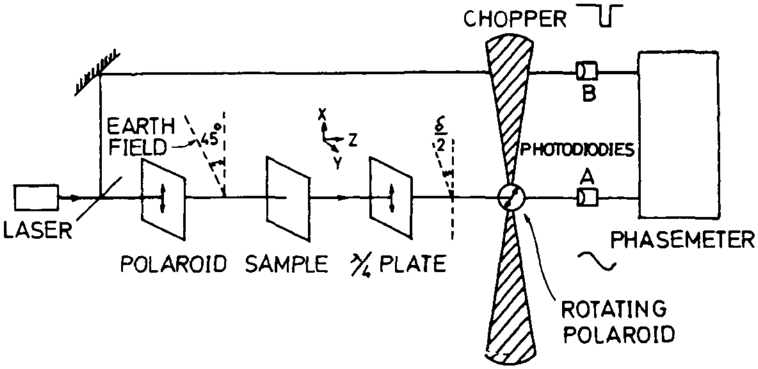
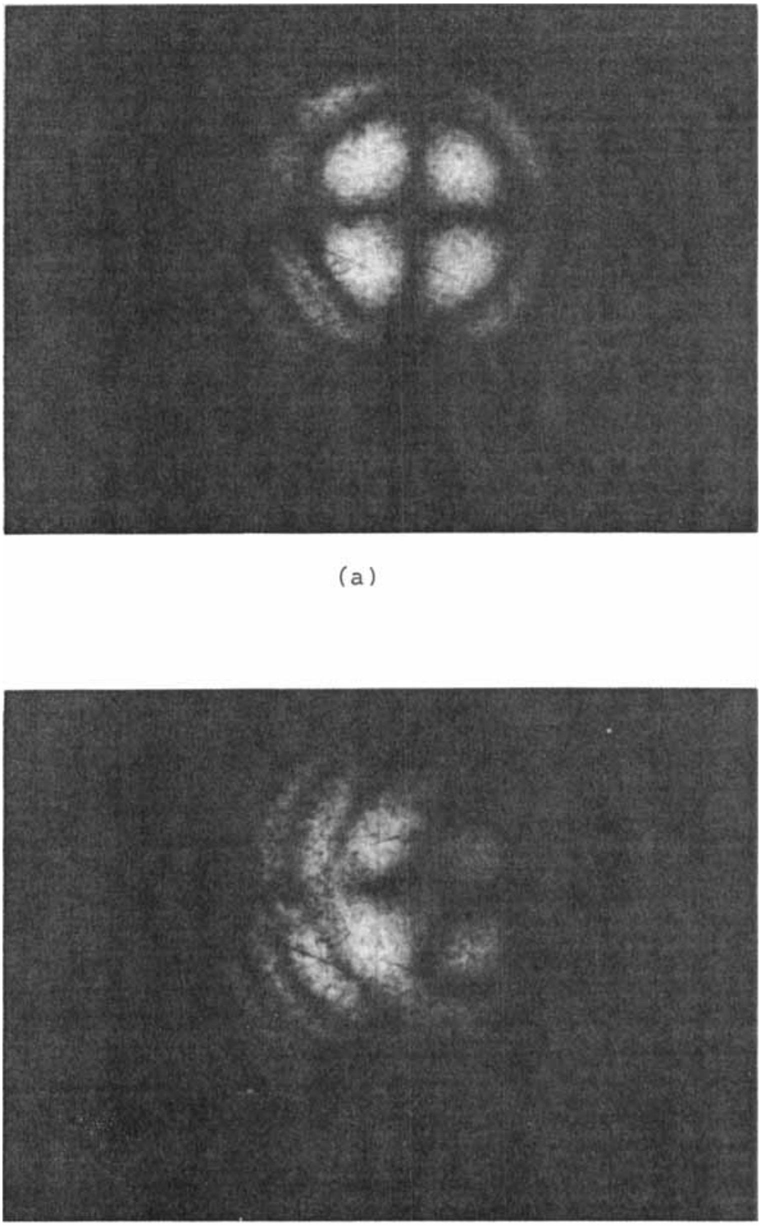


FIGURE 2 The birefringence measurement setup.

laroid before reaching the photodiode A. The reference beam passed through the chopper which had a frequency of 13.25 Hz, then was detected by photodiode B. The homeotropic film was placed horizontally with the unperturbed liquid crystal director vertically (in $\hat{z}$ direction) and an external field was applied vertically by a pair of Hemholtz coils. The polarization of the probe beam made a 45 degree angle with the horizontal component of the earth field which aligned the magnetization M of the sample in its direction. The axis of the quarter-wave plate is adjusted to be along the laser polarization direction. It was shown by Ho[6] that the phase difference δ of the extraordinary ray and ordinary ray of the probe beam after passing through the sample was equal to the relative phase difference of the sinusoidal time dependent wave from the probe beam and square wave from the reference beam which were detected by the detectors A and B, respectively. The relative phase between these two beams was measured with a sensitive phasemeter and was digitally displayed or logged.

EXPERIMENTAL RESULTS

The homeotropic aligned sample was dark when examined through a crossed polarizing microscope. With the analyzer of the microscope at 45 degree with respect to the horizontal component of the earth field, which is the unperturbed direction of M, and upon the application of a weak vertical external magnetic field H ($\sim$ a few gauss) such that $\vec{H} /\!/ \hat{n}$, the entire matrix with chiral molecules and magnetic grains exhibited strong uniform birefringence similar to the collective



(b)

FIGURE 3 The conoscopic fringe pattern (a) H = 0 (b) $H \sim 1.5$G. Color Plate III, see color plate section.

behavior observed for no-chiral-molecule matrix in previous work.[2] The same sample configuration was also inspected by conoscopy. The sample exhibited a good uniaxial crystal fringe pattern as shown in Figure 3(a). Upon the application of external magnetic field ($H \sim 1.5$G) the whole fringe shifted to the horizontal component of the earth field as shown in Figure 3(b). This confirmed the perpendicular relation of $\vec{M}$ and $\hat{n}$ and the collective behavior observation.

The birefringence measurement results are shown in Figure 4 and Figure 5. Figure 4 shows the magnetic field strength (H) dependence of the square root of the change of phase difference (δ) of the E-ray and O-ray of the probe beam after passing through the sample film for several different concentrations of CN in the mixture with fixed thickness (D = 215 μm) of the sample. Figure 5 shows $\sqrt{\delta}$ versus H for different thickness of the sample with fixed concentrations of CN.

The slopes of the linear regression of the data in the low field regime in Figure 4 versus the concentration of CN is shown in Figure 6. In Figure 7, ln $\sqrt{\delta}$ is plotted versus ln D from the data in Figure 5 with a fixed magnetic field strength (H = 1G).

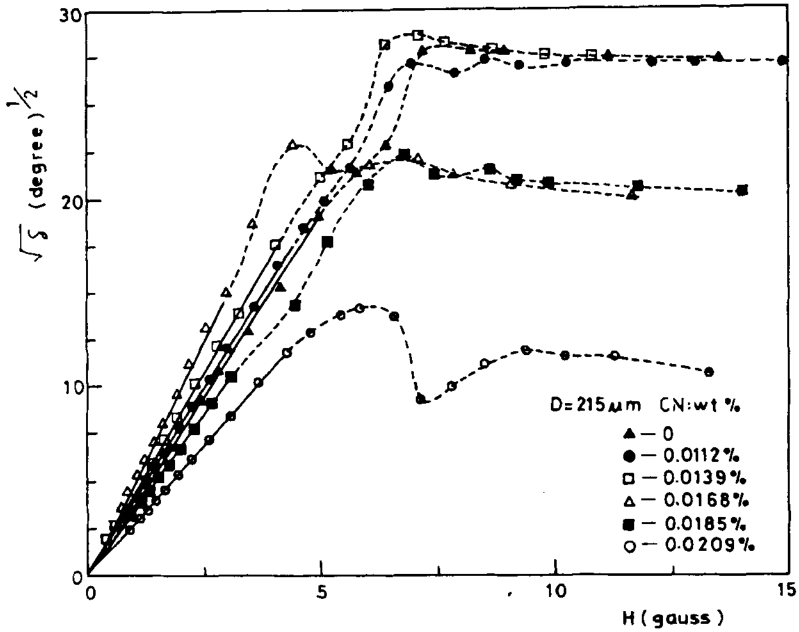


FIGURE 4 The phase difference as a function of H for different concentrations of CN.

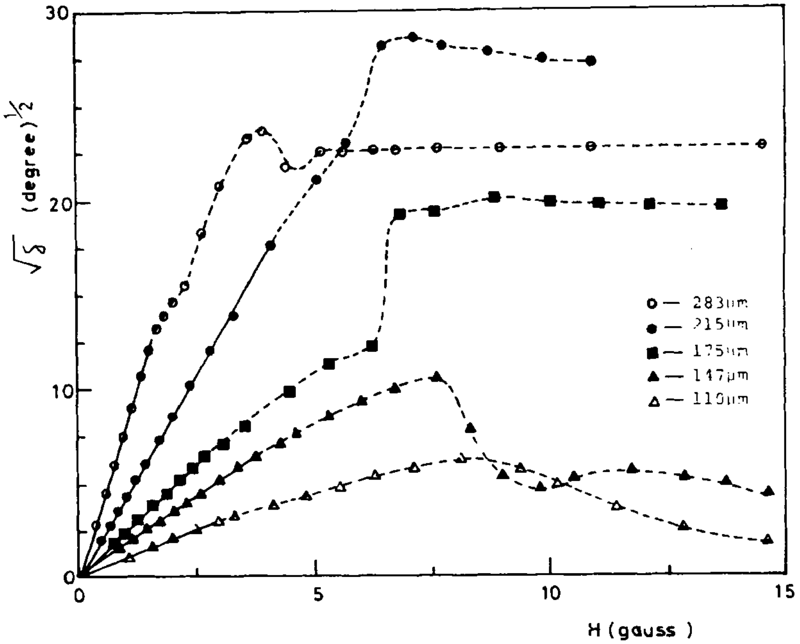


FIGURE 5 The phase difference as a function of *H* for different sample thickness.

DISCUSSION AND CONCLUSION

A general feature of the dependence of δ on H in Figure 4 and 5 is that the curves can be divided into two regimes, low fields and high fields, respectively. At low fields, there is a regime where δ, which is a measure of the nematic orientational distortion, varies monotonically with the strength of the applied field. Equation (5) predicts that $\delta \propto H^2$. It is obvious, for small distortions, the measured phase difference δ is indeed proportional to the square of the applied field. One other prediction of Equation (5) is that the phase difference is proportional to the fifth power of the thickness of the nematic matrix. Again as can be seen in Figure 7 for small distortion the experimental results are in excellent agreement with the theoretical prediction. At higher fields, as the magnetic grains begin to flocculate into clumps, a saturation regime is reached where the δ dependence on H saturates in an oscillatory fashion. In this regime the cellular texture, which was first observed in previous work[2] appeared also in this work when it was examined with a polarizing microscope.

Since the phase difference δ is proportional to the magnetization of the sample in the low field regime as predicted by Equation (5), one can find M from the slopes of the linear parts of the curves in Figure 4, for given the values of k_{33}, λ, D and the difference of n_e and n_o. For the sample of no CN, given $k_{33} = 5 \times 10^{-7}$ dyne, $D = 2.15 \times 10^{-2}$ cm, $= 6.328 \times 10^{15}$ cm and $n_e - n_o = 0.2$, we found $M = 3.029 \times 10^{-4}$ erg/G-cm^3. From the filling factor and the saturation magnetization of the magnetic particle we found $M_0 = fM_s$ giving a value of $M_0 = 1.92\ 10^{-2}$ erg/G-cm^3 for saturation magnetization of the whole matrix. By comparing M and M_0, one obtains the ratio being 0.0158. We conclude that in addition to single-magnetic particle grains there are also multiple-magnetic-particles grains which were not aligned uniformly. A matrix with single-magnetic-

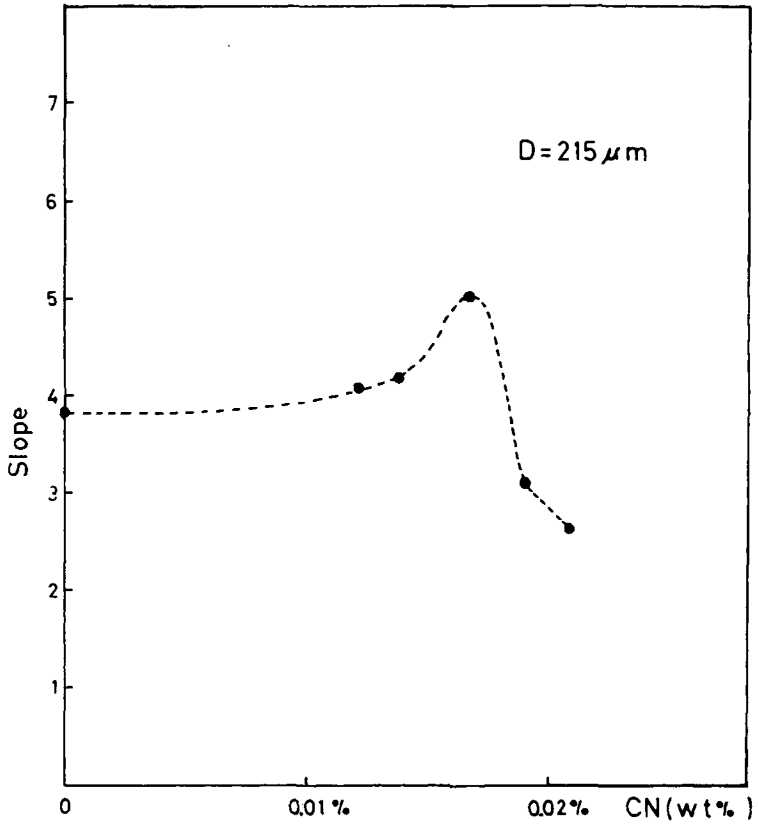


FIGURE 6 The slope of curves from Figure 4.

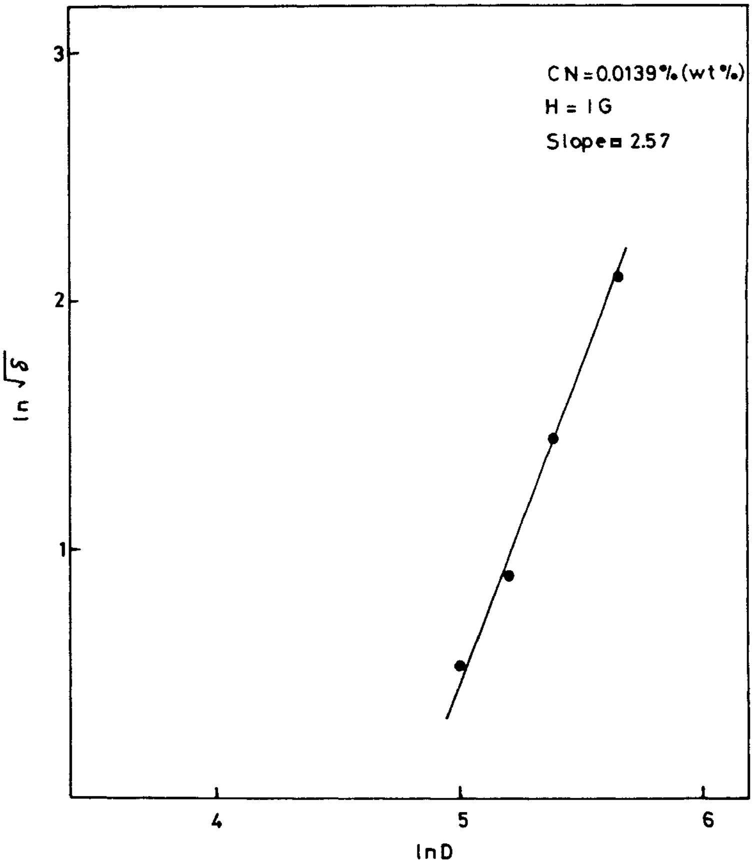


FIGURE 7 The phase difference dependence on sample thickness.

particle grains only or with uniformly aligned multiple-magnetic-particles grains would give an unity ratio of M to M_0.

Knowing the value of M for the CN-free sample, with $\delta = 100$ degree (1.745 rad) at $H = 2.5$G from Figure 4, one finds $\vartheta_M = 8.75$ 10^{-2} rad from Equation (4). This is consistent with the theory for $\vartheta_M << 1$ in low field regime.

For the samples with CN, we treated the elastic constants in the theory as effective elastic constants. From Figure 4, one can find the effective bend elastic constant k_e from the relation k_e/k_{33} = the ratio of the slope of the curve of the sample without CN to that of the sample with CN. The results is shown in Table I and Figure 6. As one can see in Table I, the effect of the chiral molecules appears in the effective elastic constant, k_e, which decreases and then increases,

TABLE I

The effect of CN molecules, the ratio of effective elastic constant to the elastic constant of plain MBBA

CN wt %	0	0.0112%	0.0139%	0.0168%	0.0185%	0.0209%
Slope	3.82	4.08	4.17	5.03	3.31	2.66
K_e/K_{33}	1	0.94	0.92	0,76	1.15	1.44

with respect to the increasing of the concentration of the chiral molecules CN.

We propose that there are two factors which influence the homeotropic alignment. The first one is the boundary condition determined by the coating of the substrate and its interaction with the liquid crystal molecules. The other one is the intrinsic property of the matrix which includes the host molecules MBBA and the guests magnetic grains and chiral molecules CN. The chiral molecules with its intrinsic helical aligning ability will inhibit the homeotropic alignment which explains the decreasing of k_e with increasing the concentration of CN. The increasing of k_e with increasing of CN concentration can be explained by disclinations formed during the sample film preparation. These disclinations help the clumping of the magnetic grains which decreases the magneto-optic effect and overcomes the influence of the former factor resulting in k_e increase with the increasing of CN. In the mean time, the nematic liquid crystal with chiral molecule has a limitation with its thickness D and natural pitch P for the homeotropic alignment namely $P/D > 3$. This means that the hometropic aligned sample will not be easy to obtain for thick samples or samples with high concentration of chiral molecules. The former decrease the boundary substrates effect and the latter inhibit the nematic property.

In order to get uniform molecular reorientation throughout the whole liquid crystal matrix, the low magnetic field regime was emphasized in our experiments and this requires a thick sample to have significant phase difference. From the above discussion it is obvious that we were limited to samples of low CN concentration. The study of electric field effects on this sample should be interesting since, without magnetic field, the sample will last longer without clumping. This makes experiments of high concentration possible which will help in understanding the effects of chiral molecules on the ferronematic sample. The investigation of the homogeneous samples of the same mixture is currently proceeding in our laboratory. The plane texture of ferrocholesteric sample of large pitch was found to be very difficult to prepare. Further work on this mixture should be helpful for the study of ferrocholesteric liquid crystals.

References

1. L. F. Brochard and P. G. de Gennes, *J. Phys.* (Paris), **31**, 691 (1970).
2. S.-H. Chen and N. M. Amer, *Phys. Rev. Lett.*, **51**, 2298 (1983).
3. H. P. Hinov and E. Kukeva, *Mol. Cryst. Liq. Cryst.*, **190**, 203 (1984).
4. H. Arnould and F. Rondelez, *Mol. Cryst. Liq. Cryst.*, **26**, 11 (1974).
5. C. F. Hayes, *Mol. Cryst. Liq. Cryst.*, **36**, 245 (1976).
6. K. C. Lim and J. T. Ho, *Mol. Cryst. Liq. Cryst.*, **47**, 193 (1978).
7. P. Pieranski, F. Brochard and E. Guyon, *J. Phys.* (Paris), **34**, 35 (1973).
8. F. J. Kahn, *Appl. Phys. Lett.*, **22**, B86, 1973.