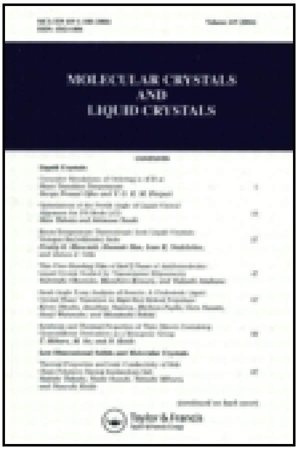

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Rotational Viscosity (γ_1) Study of Nematic Phases in Binary Liquid Crystal Mixtures of 6OCB and 8OCB

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Rotational Viscosity (γ_1) Study of Nematic Phases in Binary Liquid Crystal Mixtures of 6OCB and 8OCB

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Rotational viscosity coefficient is measured in different nematic phases of a binary liquid crystal system 6OCB–8OCB, as a function of relative concentration of the constituents, and of temperature at each concentration, using a transient NMR technique. Experiments are performed on four such mixtures with relative concentrations chosen such that for two of them there is a re-entrant nematic phase with an intervening smectic A phase (high temperature (HN) and re-entrant (RN) nematic phases), whereas for the other two there is only a single nematic phase (SN). Variation of γ_1 with concentration and temperature is distinct in the HN and RN phases, while the corresponding behaviour in the SN phase is qualitatively the same as that in the RN phase. The variation of activation energies in all the phases as a function of the relative concentration further confirms this observation. It is suggested that the dynamics in HN phase is influenced by the smectic order fluctuations remnant in the system due to the underlying smectic phase, and hence is dynamically different from the SN and RN phases, which are obtained by direct melting of the solid.

Keywords: NMR, rotational viscosity, binary liquid crystal mixture, re-entrant nematic phases.

1. INTRODUCTION

Since the first report of a reentrant nematic (RN) phase in binary liquid crystalline mixtures, Hexyloxycyano biphenyl + Octyloxycyano biphenyl (6OCB–8OCB),[1] this phenomenon has been a subject of extensive study both by experimental as well as theoretical techniques,[2,3] but the present understanding of this phenomenon still is not complete. There have been some high resolution X-ray scattering studies[4,5] and birefringence studies[6] on 6OCB–8OCB mixture which seem to be suggesting that the nematic to smectic A (N–A), and A–RN phase transitions are identical in their characteristics. Capillary shear flow studies[7] and ESR studies[8] also result in similar conclusions, in addition to finding that the dynamic behavior of normal nematic phase and RN phase are qualitatively similar. The present study is aimed at an understanding of the dynamic behavior of the two phases at a more quantitative level.

The hydrodynamics of nematic liquid crystals, made up of long rod like molecules, is adequately described by five viscosity coefficients, as introduced in the continuum theory due to Leslie[9] and Ericksen[10]. Of the five viscosity coefficients, rotational viscosity (γ_1), which has no counterpart in isotropic fluid, is an important dynamic property of the liquid crystal. There have been a number of studies[10–24], which were aimed at understanding the temperature, pressure and density dependences of γ_1, its critical behavior at N–A transition, its variation as a function of molecular structure in a homologous series, and its dependence on the composition of a mixture of liquid crystals as well as of liquid crystals with non-mesogenic compounds. γ_1 is also measured in the smectic A phase of a binary mixture of 6OCB–8OCB, exhibiting a RN phase, using pulsed NMR technique.[25] These studies show that γ_1 is large in the middle smectic phase and starts decreasing near nematic and RN phases. But there do not seem to be any measurements of γ_1 in nematic and RN phases in compounds exhibiting RN phase. This paper reports the measurements of γ_1 in binary mixtures of 6OCB–8OCB in different nematic phases. Two compositions which permit RN phase and two compositions without RN phase are studied as a function of temperature.

2. EXPERIMENTAL DETAILS

The experimental technique adopted to measure γ_1 is a relaxation method using a pulsed NMR spectrometer.[26] This technique consists of suddenly rotating a well aligned nematic sample, along an axis perpendicular to the magnetic field (H_0), and observing the relaxation of the director by recording the proton NMR spectra at regular intervals. The NMR spectra of these compounds consists of side bands, the distance between which is dependent on the nematic order parameter S as well as the orientation of the nematic director with respective to H_0. These side bands in these compounds, which arise due to the dipolar interactions between ortho protons in the core (Pake doublets), can be used to find the angle between the nematic director and H_0. If the angle of rotation (α) of the nematic director, from its equilibrium direction (the direction of the magnetic field) is less than 45°, its relaxation is governed by[26]

$$\tan[\alpha - \theta(t)] = \tan\alpha \exp(-t/\tau_0), \tag{1}$$

where $[\alpha - \theta(t)]$ is the instantaneous angle made by the nematic director with the magnetic field and,

$$\tau_0 = \frac{\gamma_1}{\chi_a H_0^2} \tag{2}$$

where χ_a is the anisotropy in the diamagnetic susceptibility of the liquid crystal. The Pake doublet splitting of the proton NMR signal of such an aligned liquid crystal at any given instant after the sample is rotated is a measure of $[\alpha - \theta(t)]$.

A home built pulsed NMR spectrometer at 20 MHz was used to record the free induction decay (FID) signals as a function of time after the sample is rotated by an angle α. The precise rotation of the sample was achieved through the use of a stepper motor arrangement. The sample rotation was synchronized with the rf pulse sequences employing a microprocessor. These FIDs were later Fourier analyzed to obtain Pake splittings. Signal averaging was done for each time delay 't' to improve the signal to noise ratio. The value of χ_a's for 6OCB and 8OCB are reported by Bradshaw *et al.*[27] Their results show that χ_a for these two compounds are same within 10%, at any given reduced temperature and vary in the same fashion with reduced temperature. At any

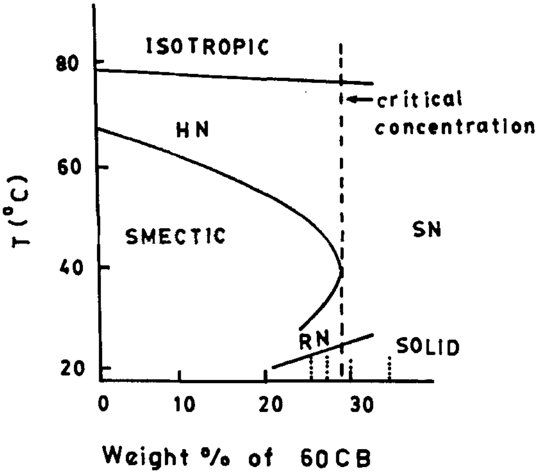

FIGURE 1 Phase diagram of the binary liquid crystalline mixture. The four compositions used in the present studies (25, 27, 30, and 35 weight % of 6OCB in 8OCB) are indicated by the vertical dotted lines.

given temperature, an average value of χ_a, of these two compounds, is used to find the value of γ_1 from Equations 1 and 2 for these binary mixtures. The accuracy in γ_1 thus obtained is about 5%.

Four compositions of the binary mixtures of 6OCB–8OCB, as shown in the Figure 1, were prepared using commercially available (BDH) compounds without further purification. Temperature was varied using a gas flow type cryostat and is stable to within 0.5 K.

3. RESULTS AND DISCUSSION

The variation of γ_1 with concentration and with temperature is shown in Figures 2 and 3. As can be seen from these figures, γ_1 is in the range of few poise in these compounds which is about three orders of magnitude less than the value reported for the S_A phase in these compounds.[25] To be able to distinguish between different nematic regions in the phase diagram (Figure 1) the following notation is used in this discussion. The high temperature nematic phase, for the concentrations resulting in RN phase (i.e., below critical concentration), is denoted by HN phase. The nematic phase, above critical concentration where a single nematic phase is observed, is denoted by SN phase.

The variation of γ_1 with concentration (Figure 2) at low temperatures, involving RN and SN phases, is weak, but γ_1 uniformly decreases with the increase in the concentration of 6OCB. The dependence of γ_1 on conentration is generally influenced by two factors,[20] viz., (i) volume effects and intermolecular forces and (ii) the variation of order parameter (S) with the concentration. In systems like 6OCB and 8OCB, whose clearing points are not very different (77 and 80°C respectively), concentration dependence of S should be very little, if the temperature dependence of the order parameter is assumed to be a universal function of reduced temperature. In that case, it is shown in the case of

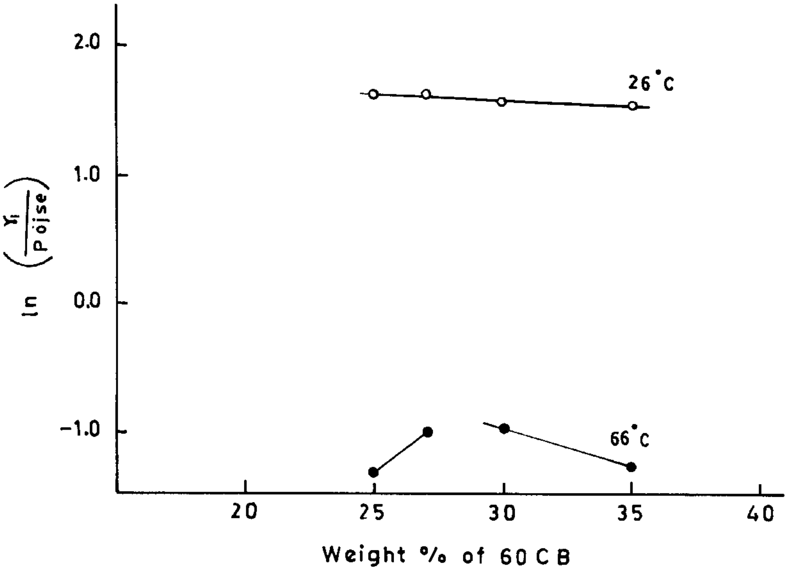

FIGURE 2 Variation of $\ln(\gamma_1)$ with weight % of 6OCB in 8OCB at different temperatures. Solid lines are guide to the eye.

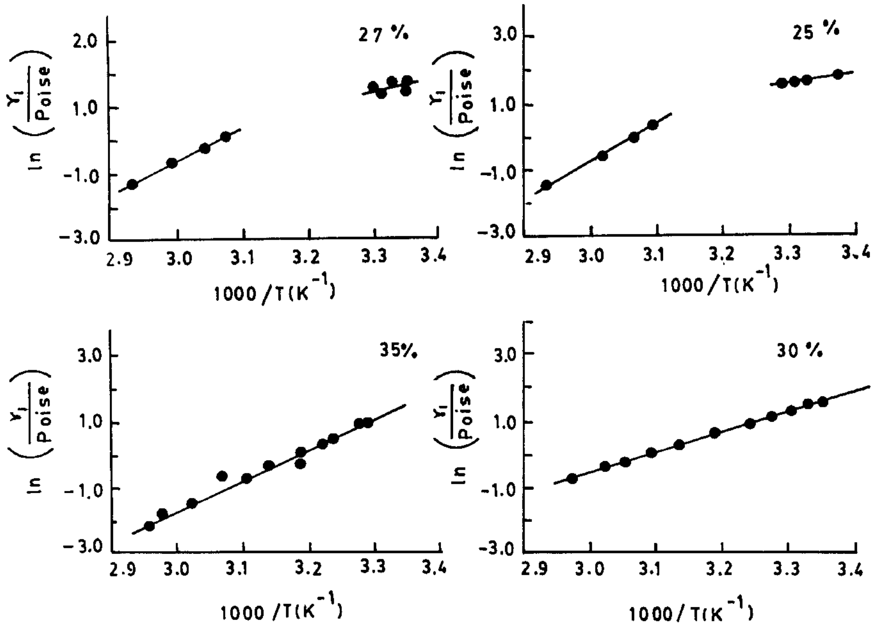

FIGURE 3 Variation of $\ln(\gamma_1)$ with $1000/T$ for four different compostions of binary mixture of 6OCB–8OCB. Solid lines are best fit Arrhenius curves.

MBBA and EBBA mixture that γ_1 is a nonlinear function of concentration and is close to a logarithmic function. Such seems to be the case in the present system as well. Also, it is found in the case of MBBA and EBBA mixture that γ_1 reduces with the increase in the concentration of MBBA, which has shorter end chains. Similar effects can be seen in the case of 6OCB–8OCB mixture.

But at higher temperatures, involving HN phase, γ_1 is more strongly concentration dependent and does not seem to be varying uniformly with concentration. As can be seen from Figure 2, γ_1 initially increased with concentration in HN phase but decreased normally in SN phase. This behavior is unlike at lower temperatures where γ_1 decreased uniformly in both RN and SN phases. There seems to be no discontinuity at RN and SN phase boundary. This indicates that the dynamic environment, characterized by γ_1, is the same in both RN and SN phases, whereas HN phase is qualitatively different compared to these two phases.

Instead of comparing a temperature dependent parameter like γ_1 in differnt phases at different temperatures, it will be more appropriate to compare a temperature independent parameter associated with γ_1. The temperature dependence of γ_1 is not well established, but is found to be different in differnent cases as

$$\gamma_1 = \gamma_0 \exp(E_a/kT), \tag{3}$$

or

$$\gamma_1 = \gamma_0 S \exp(E_a/kT), \tag{4}$$

or

$$\gamma_1 = \gamma_0 S^2 \exp(E_a/kT), \tag{5}$$

where k is the Boltzmann constant and E_a is the associated activation energy. The present data are fitted to all these three expressions, making use of the values of S from the earlier work (Figure 4).[28] These S values are measured from the distance between the side bands (Pake doublets) of proton CW NMR spectra of aligned samples using a scaling factor of 5.73, calculated for a distance of 2.45 Å between the ortho protons in the core. It is found that the best fit is obtained when the Equation 3 is used indicating the Arrhenius behaviour of γ_1 in these compounds. The activation energies thus obtained for different compositions are presented in Figure 5.

It may be noted that the activation energy associated with γ_1 is much higher in HN phase compared to the RN phase in compositions showing RN phase. Even in the compositions exhibiting SN phase the activation energies are less compared to HN phase. In fact there seems to be a systematic variation of E_a with concentration, with E_a increasing with the increase in the concentration of 6OCB in RN and SN phases. The variation of E_a with concentration in SN and RN phases, through the critical concentration, seem to be continuous, whereas HN phase shows much higher E_a and also opposite trend with composition, viz. decreasing E_a with increasing concentration of 6OCB.

These observations lead to the following conclusions. RN and SN phases seem to be having very similar dynamics but for the continuous variation brought about by the change in the composition in the binary mixture as explained above. On the other hand, HN phase has qualitatively different dynamics. This could possibly be explained as due

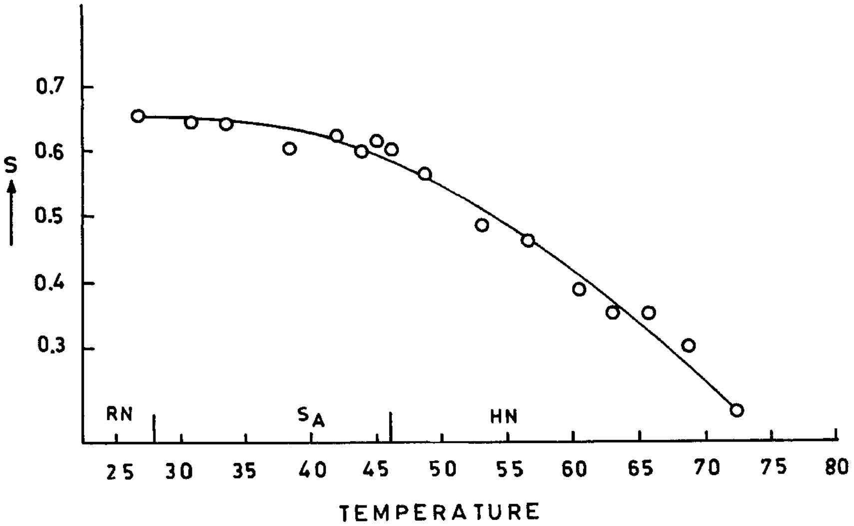

FIGURE 4 Variation of nematic order parameter (S) with temperature in a binary mixture of 25 weight % of 6OCB in 8OCB taken from Reference [27]. Solid line is a guide to the eye.

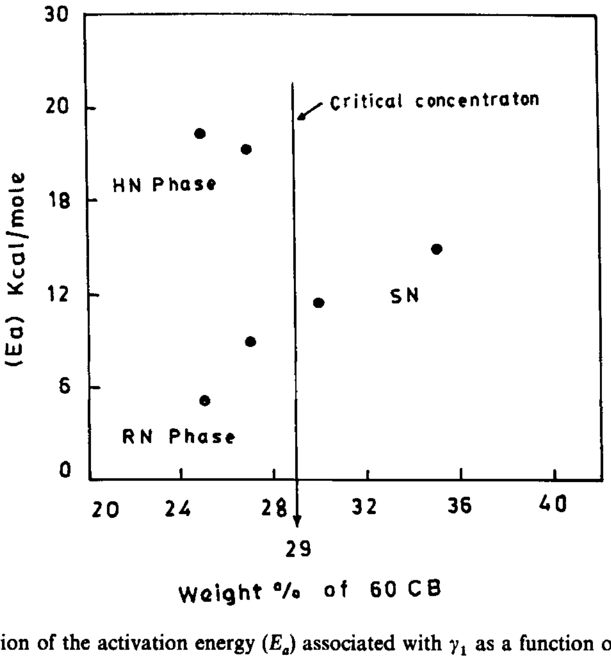

FIGURE 5 Variation of the activation energy (E_a) associated with γ_1 as a function of concentration of 6OCB in 8OCB.

to the fact that HN phase has formed due to the melting of bilayer smectic A phase, while such is not the case in the other two phases. It could be argued that, in such cases, smectic order fluctuations exist deep into the corresponding nematic phase (HN) and these smectic fluctuations make the γ_1 process more hindered. On the other hand, RN and SN phases have been formed due to the melting of the same crystalline phase and hence γ_1 behavior is expected to be the same in these two phases.

Acknowledgements

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