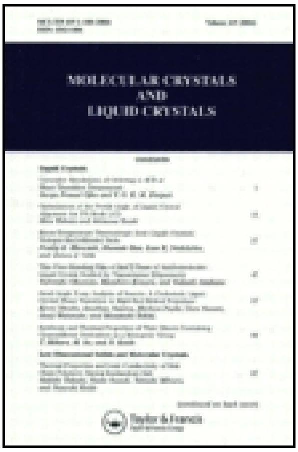


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Rotational Viscosity Measurement of a Binary Mixture Showing Both Induced Smectic and Re-Entrant Nematic Phases

Malay Kumar Das [a] & Akhileswar Prasad [a]

[a] Department of Physics, University of North Bengal, Siliguri, Darjeeling, India

Version of record first published: 14 Jun 2011

To cite this article: Malay Kumar Das & Akhileswar Prasad (2011): Rotational Viscosity Measurement of a Binary Mixture Showing Both Induced Smectic and Re-Entrant Nematic Phases, Molecular Crystals and Liquid Crystals, 540:1, 162-168

To link to this article: http://dx.doi.org/10.1080/15421406.2011.568818

Mol. Cryst. Liq. Cryst., Vol. 540: pp. 162–168, 2011

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.568818

Rotational Viscosity Measurement of a Binary Mixture Showing Both Induced Smectic and Re-Entrant Nematic Phases

MALAY KUMAR DAS AND AKHILESWAR PRASAD

Department of Physics, University of North Bengal, Siliguri,
Darjeeling, India

The rotational viscosity has been measured in a binary system of two polar nematic compounds, exhibiting nematic – smectic A_d – re-entrant nematic phase sequence. In both the nematic and re-entrant nematic phases, the rotational viscosity values are about 0.5 Pa s and show small temperature dependence. However, in the smectic A_d phase, the rotational viscosity values initially increase with decrease in temperature to attain a maximum near the middle of the smectic phase and then decreases with further decrease in temperature. The activation energies associated with rotational viscosity for the nematic phase are distinctly higher than those obtained for the re-entrant nematic phase.

Keywords Induced smectic phase; re-entrant nematic phase; relaxation time; rotational viscosity

1. Introduction

Recently, a phase diagram of a binary system comprising of a mixture of two polar nematic compounds, one having three phenyl rings in the core, 7CPB (4-cyanophenyl [4′ (4″-n-heptylphenyl)] benzoate and the other, a two phenyl ring compound 9.CN [4-cyanophenyl 4-nonylbenzoate] has been reported by us [1]. This phase diagram is marked by the appearance of an induced smectic A_d phase in the shape of an elliptical island surrounded by a nematic sea i.e., both the induced smectic and re-entrant nematic phases appear in such mixtures. Moreover, for a certain concentration range, the re-entrant nematic phase in these mixtures appears well ahead of the onset of the melting temperature. Hence these mixtures are very well suited for the study of physical properties, which may elucidate the formation of both the induced smectic and re-entrant nematic phases.

From a detailed study of the x-ray diffraction and refractive index measurements of this system, the Orientational Order Parameters (OOP's) have been determined in the induced smectic, normal nematic and re-entrant nematic phases and the nature of the isotropic-nematic, nematic – smectic A_d and smectic A_d – re-entrant nematic

---

Address correspondence to Malay Kumar Das, Department of Physics, University of North Bengal, Siliguri, Darjeeling – 734 013, India. Tel.: +91-353-2582605; Fax: +91-353-2699001; E-mail: mkdnbu@yahoo.com

phase transitions has also been assessed [1,2]. The visco-elastic properties of systems in which the induced smectic and re-entrant nematic phase occur seems to be scanty [3]. Moreover, we are not aware of any rotational viscosity (γ_1) measurement in binary systems where the induced smectic and re-entrant nematic phases are simultaneously present [4]. In this work we report the rotational viscosity measurement on the binary system (7CPB + 9.CN) exhibiting nematic (N)-Smectic A_d(Sm A_d) – re-entrant nematic (N_{re}) phase sequence. Moreover, activation energy measurements in the high temperature normal nematic phase and in the low temperature re-entrant nematic phase as determined from dielectric and NMR measurements have been found to give contradicting result [5,6]. Therefore, the viscosity data on this system may be utilized to comment on this discrepancy.

2. Experimental Methods

2.1. *Rotational Viscosity Measurement*

A relaxation method was used to determine the rotational viscosity, where a small voltage was applied to a homogeneously aligned liquid crystal (LC) cell to deform the nematic directors by a small angle. At time t = 0, when this voltage is removed, the molecules relax to the equilibrium state with relaxation time τ_o. For a LC inserted into a homogeneously aligned cell of thickness d, τ_o is related to the following material parameters:

$$\gamma_1 = \frac{\tau_0 K_{11} \pi^2}{d^2} \tag{1}$$

where K_{11} is the splay elastic constant coefficient and γ_1 is the rotational viscosity of the liquid crystal. The splay elastic constants of these mixtures have been determined by us from electric field induced Freedericksz transition [7].

Assuming that the LC directors are deformed on the application of voltage by a small angle, the decay time is approximated by the following equation [8].

$$\delta(t) \cong \delta_o \exp(-2t/\tau_o) \tag{2}$$

where δ_o is the total phase change of the LC cell under a bias voltage V_B. A plot of $\ln[\delta_o/\delta(t)]$ versus time is linear, with a slope equal to $2/\tau_o$, which yields the relaxation time. The accuracy of the relaxation time measurement is estimated to be ±5 ms.

A He-Ne laser beam ($\lambda = 632.8$ nm) was allowed to pass through a homogeneously aligned ITO coated LC cell (AWAT Co, Poland) placed between two crossed polarizers oriented at 45° to the director (Fig. 1). The temperature of the cell was regulated and measured by a temperature controller (Eurotherm PID 2216e) with an accuracy of ±0.1°C by placing the cell in a brass thermostat with glass windows. A voltage was applied to the cell and the transmitted light intensity was measured as a function of voltage, using a photodiode. The transmitted light intensity showed maxima and minima with the applied voltage (Fig. 2a). A voltage corresponding to the first maximum or minimum in the transmitted intensity was then applied to the LC cell. The corresponding photodiode output was displayed by a

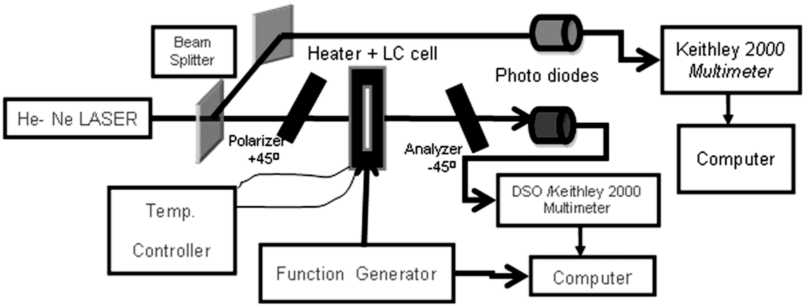


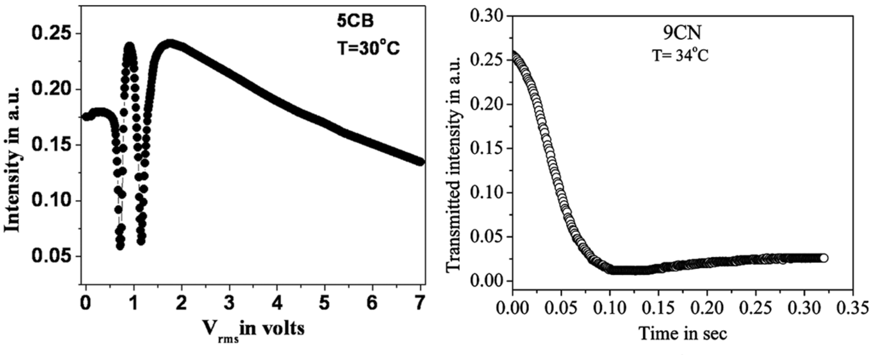
Figure 1. Schematic diagram of the experimental set-up for rotational viscosity measurement.

digital storage oscilloscope (DSO). During the relaxation process when the voltage V_B was removed at $t = 0$, the optical transmission decreases (Fig. 2b) and the phase change $\delta(t)$ could be calculated from the time-dependent intensity, I(t), according to the following equation:

$$I(t) = I_o \sin^2\{(\Delta_{tot} - \delta(t))/2\} \tag{3}$$

Where I_o is the maximum intensity change and $\Delta_{tot} = \frac{2\pi\Delta n}{d}$ is the total optical phase retardation, which was calculated from the precession birefringence measurement [2]. Once $\delta(t)$ was determined the relaxation time was ascertained from the slope of the $\ln[\delta_o/\delta(t)]$ versus time plot. Thus by measuring the relaxation time τ_o, and from the knowledge of the splay elastic constant K_{11} and the cell gap d, the rotational viscosity γ_1 can be determined.

In order to check the accuracy of our measurement, the rotational viscosity of 4-n-pentyl-4′cyanobiphenyl (5CB) were measured by us. These values were compared with those obtained by other workers [9] and are found to be in good agreement with our measurements.



(a) (b)

Figure 2. (a) Voltage dependent transmittance of 4-n-pentyl-4′cyanobiphenyl (5CB) placed inside a 8.9 μm thick homogeneously aligned liquid crystal cell at 30°C; (b) Time dependent intensity of 9.CN at 34°C, when bias voltage is removed instantaneously.

3. Results and Discussion

3.1. *Phase Diagram*

The phase diagram of the binary system 7CPB + 9.CN (Fig. 3) show an induced smectic A_d as well as re-entrant nematic phase in the concentration range $0.4 < x_{9.CN} < 0.85$, where $x_{9.CN}$ is the mole fraction of 9.CN. Interestingly, for a certain concentration range (near the eutectic point $x_{9.CN} = 0.8$), the re-entrant nematic phase in these mixtures appears well ahead of the onset of the melting temperature.

The experimentally determined relaxation times in the nematic and re-entrant nematic phases for a mixtures having $x_{9.CN} = 0.176$, 0.347, 0.471, 0.559, 0.774, 0.827 are shown in Figure 4 as a function of temperature. The relaxation times in both the N and N_{re} phases are found to be of the same order of magnitude. However, as expected, these values are always higher in N_{re} phase compared to the normal N phase. The relaxation time for mixtures having higher concentration of 9.CN is smaller with respect to those mixtures belonging to the lower concentration side of the phase diagram. It has been found that the temperature dependence of relaxation time for mixture $x_{9.CN} = 0.346$ show unusual behaviour. On reducing the temperature at about 90°C, the τ_o curve shows a steep rise up to 74°C followed by an almost equal steep fall. This may be due to the fact that the mixture at $x_{9.CN} = 0.346$ is just outside the induced SmA_d island and strong smectic fluctuations are still present in this mixture which causes to show higher values of relaxation time within a certain temperature range.

It is to be noted that we are able to determine rotational viscosity in the smectic phase of a few mixtures of which $x_{9.CN} = 0.774$ and 0.827 is presented in Figure 4b. In the smectic phase, τ_0 attains values of about 1-2 order of magnitude higher than

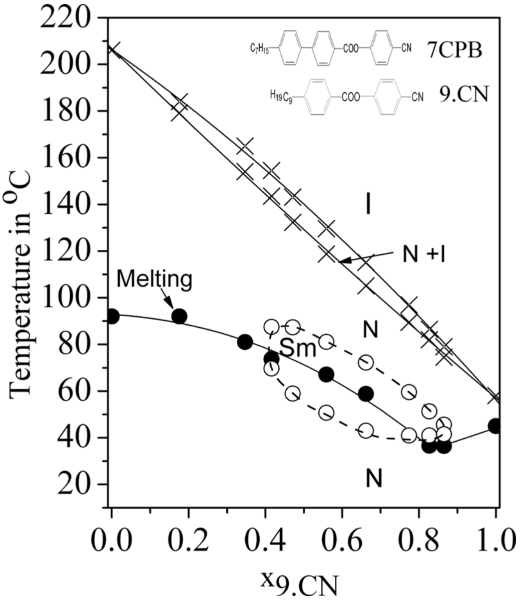
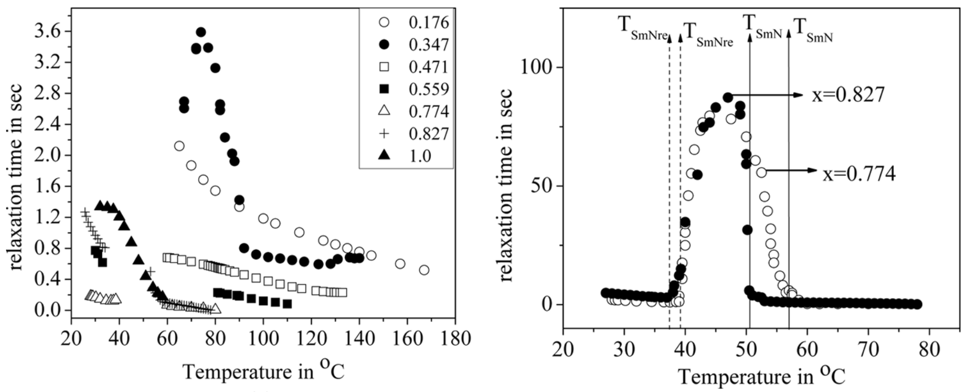


Figure 3. Phase diagram for the binary system of 7CPB + 9.CN; $x_{9.CN}$ is the mole fraction of 9.CN. I = isotropic; (I +N) = nematic-isotropic co-existing region; Sm = smectic A_d phase and N = nematic phase.



(a) (b)

Figure 4. (a) Temperature dependence of the relaxation time (τ_0) in the nematic and re-entrant nematic phases for mixtures: ○ (0.176); ● (0.347); □ (0.471); ■ (0.559); △ (0.774); +(0.827) and ▲ (9.CN); (b) Temperature dependence of the relaxation time in the nematic, smectic A_d and re-entrant nematic phases for two mixtures; $x_{9.CN} = 0.774$ (○) and $x_{9.CN} = 0.827$ (●). T_{SmN} = smectic A_d-nematic and T_{SmNre} = smectic A_d-re-entrant nematic phase transition temperatures.

those measured in the nematic phase of this mixture. Within the smectic phase, the τ_o value shows a broad maximum on varying the temperature.

The temperature dependence of rotational viscosity of a few mixtures ($x_{9.CN} = 0.176, 0.559, 0.774, 0.827, 1.0$) in the nematic and re-entrant nematic phases is shown in Figure 5. The rotational viscosity coefficient (γ_1) increases with decrease in temperature, not only in the ordinary N phase but also in the re-entrant nematic

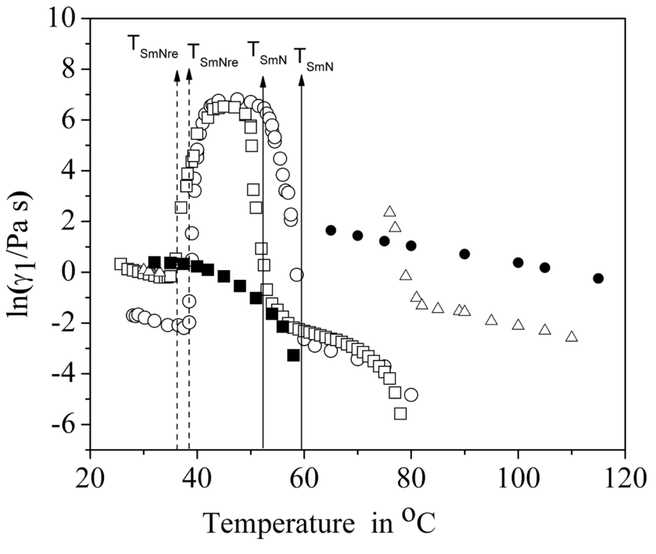
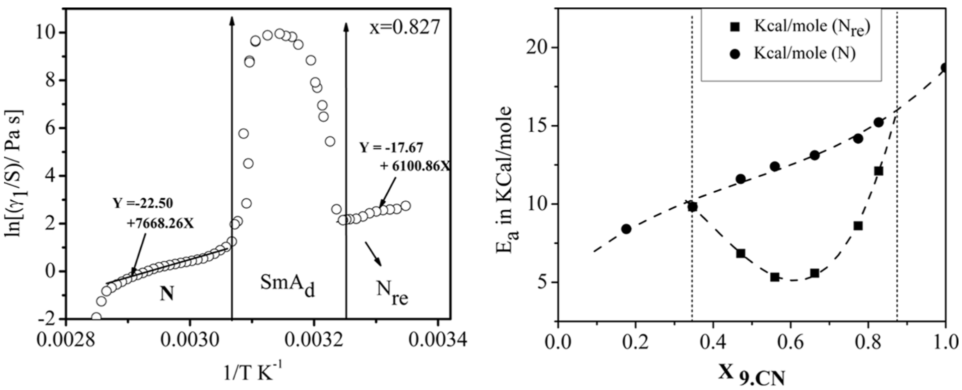


Figure 5. Temperature dependence of the rotational viscosity for mixtures: ● (0.176); △ (0.559); ○ (0.774); □ (0.827) and ■ (9.CN). T_{SmN} = smectic A_d-nematic and T_{SmNre} = smectic A_d-re-entrant nematic phase transition temperatures.



(a) (b)

Figure 6. (a) Variation of $\ln(\gamma_1/S)$ with $1/T$ for binary mixture, $x_{9.CN} = 0.827$; (b) Variation of activation energy (E_a) associated with γ_1 as a function of mole fraction of 9.CN.

phases. The rotational viscosity γ_1 in both the nematic and re-entrant nematic phases are in the range of 0.5 Pa s to a few Pa s with small temperature dependence. However, in the SmA_d phase, the γ_1 values initially increase with decrease in temperature, attain a maximum value (1000 Pa s) and then decreases with decrease in temperature and to attain a value comparable to the nematic phase values at the SmA_d-N_{re} transition temperature. Moreover, γ_1 changes continuously at the N-SmA_d and SmA_d-N_{re} transition. This behaviour is found to be consistent with the results from the birefringence, density and order parameter measurements [1,2].

The temperature dependence of γ_1 is fitted with the following expression using the values of orientational order parameter (S) from birefringence measurement [2]:

$$\gamma_1 = \gamma_0 S \exp\left(\frac{E_a}{k_\beta T}\right) \tag{4}$$

Where k_β is the Boltzmann's constant and E_a is the associated activation energy. The variation of $\ln(\gamma_1/S)$ with $1/T$ for $x_{9.CN} = 0.827$ is shown in Figure 6a. From the slope of the curve the activation energy E_a can be evaluated. The variation of activation energy (E_a) associated with γ_1 as a function of mole fraction of 9.CN is shown in Figure 6b.

It is to be noted that the activation energies associated with γ_1 for the N phase are distinctly higher than those obtained from the re-entrant nematic phase. Our results contradict the results of activation energy calculated from dielectric method [5]. However, our results do agree well with the rotational viscosity measurements of Sailaja et al. [6] on 6OCB + 8OCB binary system. There is a systematic variation of E_a with concentration. E_a increases with the increase in the concentration of 9.CN in N_{re} phase. However, the activation energies in the N_{re} phase show a local minimum around $x_{9.CN} = 0.6$ i.e., at the centre of the smectic island.

4. Conclusions

A simple electro-optical method was used to determine the relaxation time and hence the rotational viscosity, γ_1, of a binary system possessing *nematic (N)-Smectic*

A_d(SmA_d) – re-entrant nematic (*N_{re}*) phase sequence. Upon cooling, the γ_1 values not only increase in the normal N phase but also in the N_{re} phase and has same order of magnitudes about 0.5 to a few Pa s. Rotational viscosity values are about two to three order of magnitude higher in the SmA_d phase than those measured in the N phase. The activation energies for the N_{re} phase are smaller than those for the normal nematic phase. The difference $[(E_a)_N - (E_a)_{Nre}]$ is maximum near the centre of the phase diagram. This result indicates that the interaction between monomer molecules or that between dimer aggregates is weaker in the N_{re} phase than in the normal nematic phase. For normal nematic phase, the activation energy increases with an increase in mole fraction of 9.CN, while that for N_{re} phase it shows a local minimum near $x_{9.CN} = 0.6$, i.e., at centre of the phase diagram.

Acknowledgment

We gratefully acknowledge financial support from Department of Science and Technology, New Delhi (Project No: SR/S2/CMP-20/2005) and an award of research fellowship (AP).

References

[1] Prasad, A., & Das, M. K. (2009). *Phase Transitions*, *82*, 780.
[2] Prasad, A., & Das, M. K. (2010). *Phase Transitions*, *83*, 1072.
[3] Czechowski, G., & Jadzyn, J. (2004). *Acta Physica Polonica*, *106*, 475.
[4] Brodzik, M., & Dabrowski, R. (1995). *Mol. Cryst. Liq. Cryst.*, *260*, 361.
[5] Ratna, B. R., Shashidhar, R., Bock, M., Gobl-Wunsch, A., & Hepke, G. (1983). *Mol. Cryst. Liq. Cryst.*, *99*, 285.
[6] Sailaja, A. S., Venu, K., & Sastry, V. V. S. (1994). *Mol. Cryst. Liq. Cryst.*, *250*, 177.
[7] Prasad, A., & Das, M. K. to be communicated.
[8] Wu, S. T., & Wu, C. S. (1990). *Phys. Rev. A*, *42*, 2219.
[9] Dark, M. L., Moore, M. H., Shenoy, D. K., & Shashidhar, R. (2006). *Liq. Cryst.*, *33*, 67.