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Temperature Dependence of Visco-Elastic Properties of 5CB

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Visco-elastic properties of 5CB as a function of temperature in the nematic region are studied. Three Miesowicz viscosity coefficients η_a, η_b and η_c and rotational viscosity γ_1 are determined by dynamic light scattering (DLS) measurements. By assuming $\alpha_3 \cong 0$, other Leslie viscosity coefficients are also calculated. Fitting our γ_1 data to Osipov and Terentjev's theory, a coupling constant of $3.14k_BT_c$ is obtained, which is smaller than the mean field theory value. Temperature dependence of order parameter is obtained from refractive index measurement using Haller's method. To obtain accurate viscosity parameters from DLS, accurate values of elastic constants are required. Three different techniques are used to determine K_{11}, K_{22} and K_{33}, respectively: fitting the electric field dependence of capacitance to nematic continuum theory, ac electric field DLS and magnetic Freedericksz transition.

Keywords: dynamic light scattering; visco-elastic properties; 5CB

INTRODUCTION

Visco-elastic properties of nematic liquid crystals(NLCs) play an important role in characterizing liquid crystal displays and therefore their determination is practically important. These properties are also theoretically interesting since viscosity is one of the least understood areas in nematics. Attempts[1-5], both theoretical and experimental, to understand the origin of LC viscosity have been made, but a satisfactory agreement hasn't been reached. Rotational viscosity is a very important parameter for LC applications since it directly determines the response time of LC devices. It is generally suggested that the temperature dependence of the rotational viscosity is likely to be of the form

$$\gamma_1 \sim S^{\beta} \exp[E(S)/k_B T] \qquad (\beta=0, 1, 2) \qquad (1)$$

with E(S) the activation energy and S the nematic order parameter. In this paper we test our γ_1 data with this expression and will give some discussions. Our rotational viscosity data fit well to the microscopic theory developed by Osipov and Terentjev[2] in 1989 (abbreviated as the OT theory) for describing the origins of LC viscosities.

Several methods[1,6] have been developed to measure the viscosities and elastic constants of NLCs. In this paper we report our measurement results of three Miesowicz viscosities η_a, η_b and η_c and rotational viscosity γ_1 of 5CB by DLS technique. We compare our results with those previously determined from shear flow experiments and good agreement is obtained[7,8]. Taking $\alpha_3 \cong 0$ for 5CB[7] and Parodi's relation, other Leslie viscosity coefficients, except α_1, are also calculated and compared.

DYNAMIC LIGHT SCATTERING

Orsay theory[9] predicted that an incident laser beam will receive a Lorentzian broadening due to scattering from two overdamped modes within the nematic medium. The mean relaxation frequencies of the two modes can be determined by photon correlation analysis and are given by

$$\Gamma_v(q) = \frac{(K_{33} q_{//}^2 + K_{ii} q_\perp^2)}{\eta_v(q)} \qquad (2)$$

where $\eta_v(q)$ are two viscosity functions:

$$\eta_1(q) = \gamma_1 - \frac{(q_\perp^2 \alpha_3 - q_{//}^2 \alpha_2)^2}{q_\perp^4 \eta_b + q_\perp^2 q_{//}^2 (\alpha_1 + \alpha_3 + \alpha_4 + \alpha_5) + q_{//}^4 \eta_c} \qquad (3)$$

$$\eta_2(q) = \gamma_1 - \frac{q_{//}^2 \alpha_2^2}{q_\perp^2 \eta_a + q_{//}^2 \eta_c} \qquad (4)$$

α_i refer to the five Leslie viscosity coefficients, γ_1 the rotational viscosity, and η_a, η_b and η_c the Miesowicz viscosities. q is the scattering vector and the subscripts // and $\perp$ denote directions parallel and perpendicular to the nematic

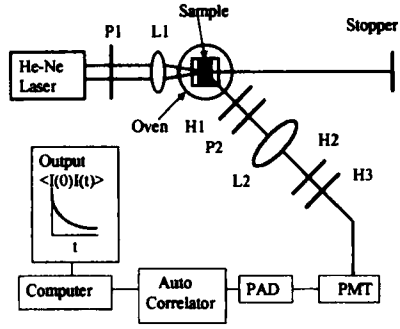

FIGURE 1 Experimental set-up for DLS. P1, P2 -- polarizer and analyzer; H1, H2, H3 -- variable apertures; PMT -- photomultiplier tube; L1, L2 -- lens; PAD -- pulse amplifier discriminator.

director. These modes contain mixed director deformations. By choosing appropriate combinations of scattering angle, polarization of incident and scattered light, and director orientation, these modes can be decoupled to pure deformations and the expressions are simplified.

As shown in Fig.1, photon correlation analysis of the scattered light was performed by an instrument equipped with a 10mW He-Ne laser and a BI-9000AT 256-channel digital autocorrelator (Brookhaven Instruments Corp., Holtsville, NY). The sample was placed inside a custom-designed oven which was temperature controlled by LakeShore 330 autotuning temperature controller with accuracy of ±0.1°C. The optical system for detecting the scattered light is mounted onto a rotating arm controlled by a stepper motor with a resolution of 0.02° purchased from Oriel.

Two different scattering geometries[6,10,11] are used in our experiments. Geometry A utilizes a homogeneously aligned sample with the director perpendicular to the scattering plane. The normal incident light is polarized parallel to the director and the scattering light is polarized in the scattering plane. In this way, the two modes are decoupled to pure splay and pure twist deformations, respectively. Further at the so called magic angle, by setting the geometry factor of pure twist mode be zero, only pure splay mode is sampled in the experiment. The decay rate becomes

$$\Gamma_1 = K_{11} q_\perp^2 / \eta_{splay} \tag{5}$$

where

$$\eta_{splay} = \gamma_1 - \alpha_3^2/\eta_b \cong \gamma_1 \tag{6}$$

To get better statistics, we use the data in a 5° range around the magic angle to linearly fit Γ_1 with $q_\perp^2$ to get the value of K_{11}/η_{splay} . In this range of scattering angles the mode mixing is less than 0.1%.

Geometry B also uses a homogeneously aligned sample and the polarization directions of the incident and the scattered light are the same as geometry A, but the director is parallel to the scattering plane. Then only the mode with coupled twist and bend deformations remains since the geometry factor of the other mode vanishes. Again at the magic angle this mode becomes a pure bend deformation with

$$\Gamma_2 = K_{33} q_{//}^2/\eta_{bend} \tag{7}$$

$$\eta_{bend} = \gamma_1 - \alpha_2^2/\eta_c \tag{8}$$

and again the linear fit is used to get the value of K_{33}/η_{bend}.

Using the results obtained above, η_c / α_2^2 can be determined by fitting the viscosity function η_2 in geometry B configuration over the laboratory scattering angle range of 10°~50°.

ELASTIC CONSTANTS

Accurate values of three elastic constants are required for calculating the viscosities from DLS measurements. Different approaches have been used in this work to get K_{11}, K_{22} and K_{33}. Of the several methods to obtain the elastic constants, Freedericksz transition technique is the most commonly used and well investigated. But when the field is not oriented either parallel or perpendicular to the director, there no longer exists a threshold field. Even for a small tilt bias, there is already a rounding off at the threshold. This makes extrapolation to obtain the threshold field difficult, and leads to erroneously smaller values of elastic constants. By carefully aligning the initial director orientation, the error may be reduced to a minimum in the case when a magnetic field is used provided that accurate values of $\Delta\chi$ are available, which is generally not true. To avoid this problem, computer fitting of the electric field dependence of capacitance to the nematic continuum theory is

used in this work. The fitting is made in the range around the critical field with three parameters: pretilt, K_{11} and K_{33}. Details of the measurement and fitting procedure will be published later. This method gives accurate and reliable values for K_{11}. Alternative values for K_{33} are obtained by magnetic splay and bend Freedericksz transition measurements using K_{11} values from the fitting. In this case no $\Delta\chi$ value is needed.

Unlike K_{11} and K_{33}, the determination of K_{22} is much more difficult since the conventional Freedericksz transition technique cannot be applied. In this work, electric field DLS technique is explored and satisfactory results are obtained.

It has been shown[9,12] that when using homeotropically aligned sample with the director parallel to the incident wave vector in the geometry configuration we used above, for general scattering angles, the scattering is principally due to the twist deformation with a minor contribution from the bend deformation. At small scattering angles a nearly pure twist mode is obtained. When an ac electric field is applied along the director of NLC which has a positive dielectric anisotropy, the relaxation rate of the pure twist mode Γ_2 increases linearly with the square of the applied voltage V. K_{22} can be determined from the intersection of a plot of Γ_2 against V^2 using γ_1 value obtained from geometry A.

Results of elastic constants as a function of temperature determined by the techniques described above are shown in Fig.2. These results are in good agreement with those published in the literature[10,13].

REFRACTIVE INDICES AND ORDER PARAMETER

In addition to the elastic constants, accurate values of the refractive indices are needed to extract the nematic viscosities from DLS. Refractive indices n_o and n_e were measured using a 60/HR Abbe refractometer (Kernco Instruments Co., Inc.). The refractometer was temperature controlled by a pumped coolant-water system and the temperature is measured using a thermometer with accuracy of ±0.5°. The accuracy for the refractive index results is about ±0.001.

Data of order parameter S as a function of temperature will be needed later in this paper when we discuss the rotational viscosity because γ_1 depends not only on temperature but also on order parameter. Here we follow Haller's[14] method to determine the order parameter from nematic phase

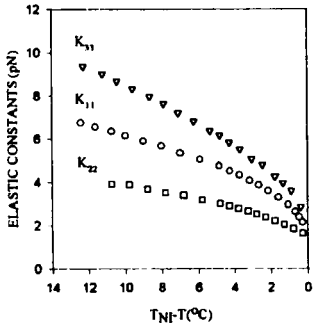

FIGURE 2 Temperature dependence of elastic constants of 5CB.

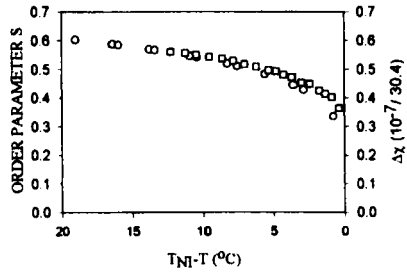

FIGURE 3 Temperature dependence of order parameter and magnetic anisotropy of 5CB. square -- $\Delta\chi$; circle -- order parameter.

refractometric data. This method uses Vuks assumption, which leads to the following relation between order parameter and refractive indices

$$\log(n_e^2 - n_o^2)/(\bar{n}^2 - 1) = C + A\log\left(1 - \frac{T}{T^*}\right). \tag{9}$$

where $\bar{n}^2 = (n_e^2 + 2n_o^2)/3$ and T^* is a hypothetical second-order phase transition temperature obtained by extrapolating the gradual decrease of the order parameter to zero. T^* is higher than the observed first-order transition temperature T_{NI}. The temperature dependence of nematic order parameter is described by

$$S = \left(1 - \frac{T}{T^*}\right)^A \tag{10}$$

Order parameter as a function of temperature obtained by fitting Eq.9 to our index of refraction data is shown in Fig.3. The exponent A is fitted to be 0.1812 and falls in the range of 0.17-0.23 found by Haller for many compounds with widely different chemical compositions. The T^*-T_{NI} value is 0.25 which yields a value of S_{NI}=0.275. This is consistent with Haller's conclusion that compounds with low nematic-isotropic transition temperatures appear to predominate among those having low S_{NI}. But all the

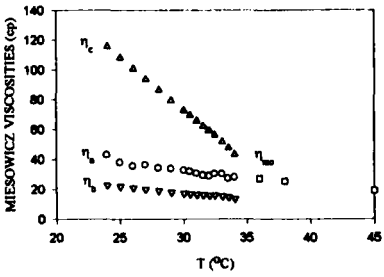

FIGURE 4 Temperature dependence of Miesowicz viscosities and viscosities in the isotropic phase for 5CB.

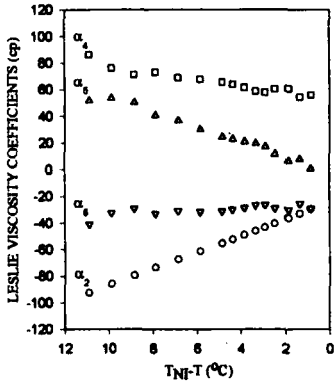

FIGURE 5 Temperature dependence of Leslie viscosity coefficients of 5CB.

materials in his paper have higher T_{NI} than 5CB. Also shown in Fig.3 is the scaled value of magnetic anisotropy $\Delta\chi$, which is obtained from magnetic splay Freedericksz transition measurement knowing K_{11} from fitting the capacitance curve. From the figure we see that the order parameter determined by Haller's method decreases faster than $\Delta\chi$ when approaching the transition.

VISCOSITIES

Based on DLS measurements and elastic constant data, three Miesowicz viscosities have been calculated and their temperature dependence results over the entire nematic range are shown in Fig.4. These results agree quite well with those obtained from slot viscometer measurement[7], which directly measures the three Miesowicz viscosities.

In Fig.4 we also show the viscosity in the isotropic phase measured with a Brookfield Digital Rheometer (Model DV-III). It follows Eyring's exponential function well and the activation energy is found to be about 0.34eV.

Assuming $\alpha_3 \cong 0$ and using Parodi's relation, values of α_2, α_4, α_5 and α_6 as a function of temperature have been calculated and are shown in Fig.5. Again, good agreement is obtained compared to the results in [7, 8] except that our α_4 values are lower and less temperature dependent at higher temperatures. One interesting feature of this figure is that as

temperature increases α_3 approaches zero more quickly than α_6. Due to lack of data at very high temperature, we do not exactly know the behavior of α_5 near the nematic-isotropic transition, but we see it tends toward zero or may become negative. To our knowledge, no existing nematic viscosity theory has ever predicted such behavior. The result of $\alpha_5 < |\alpha_6|$ near the transition temperature is inconsistent with OT theory, which predicts that the value of α_5 is always greater than the absolute value of α_6.

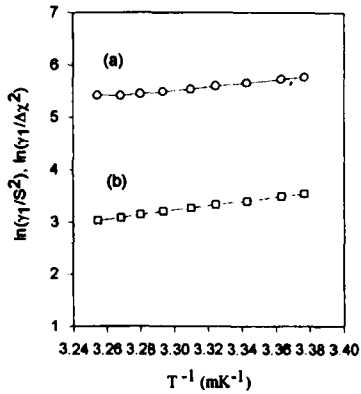

FIGURE 6 Scaled rotational viscosity vs. inverse of temperature for 5CB.
(a) -- using order parameter;
(b) -- using $\Delta\chi$.

Many different expressions have been proposed for the temperature dependence of γ_1 in nematics[1,2,5]. The commonly considered relationships are of the form given by Eq.1. The activation energy E(S) can be proportional to S according to the mean field theory or be independent of S as some experiments suggest. We test this expression using our γ_1 data and find good agreement with $\beta=2$ and E(S) independent of S, i.e.

$$\gamma_1 \sim S^2 \exp[E/k_B T] \qquad (11)$$

as shown in Fig.6. The calculated activation energies are 0.270eV and 0.366eV using order parameter and $\Delta\chi$ data respectively. The difference is caused by the discrepancy between S and $\Delta\chi$ while approaching transition temperature. But this expression is experimentally ruled out by several studies[1,15] while testing different materials; and so far no theoretical considerations which support this expression have been seen.

One of the existing nematic viscosity theories is OT theory which gives a microscopic description of the origins of LC viscosities. In this theory, the microscopic friction coefficient possesses an exponential temperature dependence with a large activation energy E_1 which is mainly determined by the isotropic part of the molecular interaction potential. This activation energy dominates the strong temperature effect on the Leslie viscosity coefficients.

The rotational viscosity is characterized by an additional exponential term with a smaller activation energy determined by the nematic mean field potential barrier J_0S and can be written as

$$\gamma_1 = F\sqrt{S}\,T^4 \exp\{[E_1+J_0S]/k_BT\} \qquad (12)$$

where F is a function of molecular parameters. Fitting our experimental data of γ_1 to Eq.12, E_1 is found to be 0.336eV and the mean-field coupling constant J_0 is $3.14k_BT_c$. The J_o result is lower than the Maier-Saupe theory value of $4.5k_BT_c$. In reference [4], the authors fit experimental data of γ_1 to OT theory with several LC materials including 5CB. They obtain $J_o=2.59k_BT_c$ for 5CB. This lower value may in part be explained by their use of T_c in Eq.10 rather than T^*.

From the above investigation on γ_1, both Eq.11 and OT theory fit well to our experimental data and the activation energies obtained in these two cases are very close. But their connection is still a question and our investigation are continuing with other materials.

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