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Rotational viscosity of nematic liquid crystals A critical examination of existing models

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A simple electro-optical method was developed to characterize the temperature dependent viscoelastic coefficient of six nematic liquid crystals with different conjugation lengths. Results were then used to test seven most frequently used models for rotational viscosity (γ_1). Computer results show that some models fit certain specific liquid crystals but, in general, two models fit all the experimental data. These two models are $\gamma_1 = \alpha_2 S^2 \exp[E/k(T - T_0)]$ and $\gamma_1 = (\alpha_1 S + \alpha_2 S^2) \exp(E/kT)$, with α_1 , α_2 , E , and T_0 as adjustable parameters.

1. Introduction

Rotational viscosity (γ_1) of an aligned nematic liquid crystal (LC) represents an internal friction among LC molecules during the rotation process. It is an important parameter in electro-optic applications employing a LC, because the response time of the LC device is linearly proportional to γ_1 . The magnitude of γ_1 of a LC depends on the detailed molecular constituents, structure, and intermolecular association. Similar to the isotropic liquid, the rotational viscosity of the anisotropic liquid crystals is also very sensitive to temperature; as temperature increases, γ_1 declines.

Several theories [1-5] and empirical formulae have been developed for describing the temperature effect of rotational viscosity. In general, these equations have the form shown below [6]:

$$\gamma_1 = f(S)g(T), \quad (1)$$

where $f(S)$ is a function of the directional order parameter (S) which, in turn, is a function of temperature (T). The order parameter decreases gradually with increasing temperature; a more drastic change occurs as T approaches T_{NI} , the nematic isotropic phase transition temperature. If we expand $f(S)$ in a power series:

$$f(S) \approx \alpha_0 + \alpha_1 S + \alpha_2 S^2 + \dots \quad (2)$$

and assuming $g(T)$ is mainly an exponential function of T with no or only a weak dependence on S , we can rewrite γ_1 in a general form like

$$\gamma_1 = (\alpha_0 + \alpha_1 S + \alpha_2 S^2) \exp \frac{ES^m}{k(T - T_0)}, \quad (3)$$

where α_i s are proportionality constants, E is the activation energy of diffusion, m is an exponent, k is the Boltzmann constant, and T_0 has a physical meaning of 'freezing' temperature for a LC. The general form of equation (3) has too many adjustable parameters to fit the experimental results.

Six special expressions simplified from equation (3) have been frequently used in previous papers to fit experimental data. In this paper, we add another one (the seventh in the list) which is modified from Imura and Okano's theoretical work [1] for comparison with the experimental results obtained from six nematic LC compounds with different conjugation lengths. These seven expressions of rotational viscosity are listed below:

$$\left. \begin{aligned}
 (1) \quad \gamma_1 &= \alpha_0 \exp(E/kT), \\
 (2) \quad \gamma_1 &= \alpha_1 S \exp(E/kT), \\
 (3) \quad \gamma_1 &= \alpha_2 S^2 \exp(E/kT), \\
 (4) \quad \gamma_1 &= \alpha_2 S^2 \exp(ES/kT), \\
 (5) \quad \gamma_1 &= \alpha_2 S^2 \exp[E/k(T - T_0)], \\
 (6) \quad \gamma_1 &= \alpha_2 S^2 \exp[ES^2/k(T - T_0)], \\
 (7) \quad \gamma_1 &= (\alpha_1 S + \alpha_2 S^2) \exp(E/kT).
 \end{aligned} \right\} \quad (4)$$

The first expression in equation (4) is the well-known Arrhenius's law for isotropic fluids. The second one has been used by DeJeu [7] to fit his results on the N-4 LC mixture (the mixture of the two isomers of *p*-methoxy-*p'*-butylazoxybenzene, E. Merck, Darmstadt). The third one, derived by Hess, [2] and the fifth one are used by Knepe *et al.* [6] to fit their results on MBBA and N-4 LC mixture. The fourth one was derived by Martins and Diogo [3] and the sixth one by Diogo and Martins [4] based upon their free volume theory. The seventh one is modified from Imura and Okano's original expression: $\gamma_1 = C_1 S + C_2 S^2$, where C_1 and C_2 coefficients. Here, an additional exponential term is introduced by us.

Solely from the thermodynamic standpoint, [8] the leading term in $f(S)$ should be the second order term, i.e. $f(S) \sim S^2$ in order to accommodate the concern that S may be negative. Nevertheless, we do not preclude the first order term in our computer fittings with experimental results. All the expressions shown in equation (4) have two to three parameters.

In this paper, we present a simple electro-optical method for determining the temperature dependent rotational viscosity. Six nematic LCs with different conjugation lengths were used for evaluation. Experimental results are then used to validate expressions listed in equation (4). In §2, the experimental technique and its theoretical background is described. Experimental results are presented in §3 and used to test theories in §4.

2. Measurement principles

2.1. Viscoelastic coefficient

Several methods have been developed for measuring the rotational viscosity (γ_1) [6, 9] or viscoelastic coefficient (γ_1/K_{11}) [10–12]. Each method has its own merit. Here we describe a simple and convenient electro-optical method for measuring γ_1/K_{11} at different temperatures. By validating that $K_{11} \sim S^2$ experimentally, we can deduce the functional dependence of γ_1 . Although this is not a direct measurement of γ_1 itself, the whole procedure is reliable as will be discussed step by step.

The relaxation dynamics of a parallel-aligned LC cell under a small voltage perturbation is well known in the literature [13]. The spatial and temporal dependence

of the director's angle (θ) is expressed as

$$\theta(z, t) \cong \theta_m \sin\left(\frac{\pi Z}{d}\right) \exp(-t/\tau_0), \quad (5)$$

where θ_m is the maximum tilt angle of the LC directors in response to the applied voltage, d is the LC thickness, Z is the position of the oriented LC layer under discussion, and $\tau_0 = \gamma_1 d^2 / K_{11} \pi^2$ is the free relaxation time of the LC layer. The time dependent phase change ($\Delta(t)$) associated with this angle change during the decay process is described as follows:

$$\Delta(t) = \frac{2\pi}{\lambda} \int_0^d \left[\frac{n_o n_e}{(n_o^2 \cos^2 \theta + n_e^2 \sin^2 \theta)^{1/2}} - n_o \right] dz, \quad (6)$$

where n_o and n_e are the refractive indices for the ordinary and extraordinary rays, respectively, and θ is that described in equation (5). Under small angle approximation, equation (6) can be expanded by a power series of θ . Substituting equation (5) into this expansion, after some algebra the transient phase change $\delta(t)$ [$\delta(t) \equiv \Delta_{\text{tot}} - \Delta(t)$] is obtained

$$\delta(t) \cong \delta_0 \exp(-2t/\tau_0), \quad (7)$$

where Δ_{tot} is the total phase retardation of the LC cell under null voltage and δ_0 represents the magnitude of the net phase change from the voltage 'on' state to the voltage 'off' state. At $t = 0$, the applied voltage is removed instantaneously and LC directors start to decay. After a sufficient time, the steady state of the null voltage state is reached and the phase difference approaches zero; i.e. $\delta(t \rightarrow \infty) = 0$. Under this circumstance, the LC cell has a total phase retardation $\Delta_{\text{tot}} = 2\pi d \Delta n / \lambda$ for an incident laser beam (λ) with its polarization axis oriented at 45° to the LC directors, and $\Delta n = n_e - n_o$ is the birefringence of the LC at wavelength λ and temperature T .

To illustrate this technique, an example is given below. A parallel-aligned LC cell consisting of BDH-E44 was made. Its thickness was measured to be $d = 8.6 \mu\text{m}$ using the interferometric method. The voltage dependent transmission of the cell under crossed polarizers at $\lambda = 632.8 \text{ nm}$ and $T \cong 22^\circ\text{C}$ is shown in figure 1. The total phase retardation of the cell is calculated to be $\Delta_{\text{tot}} = 6.73\pi$, and Δn is calculated

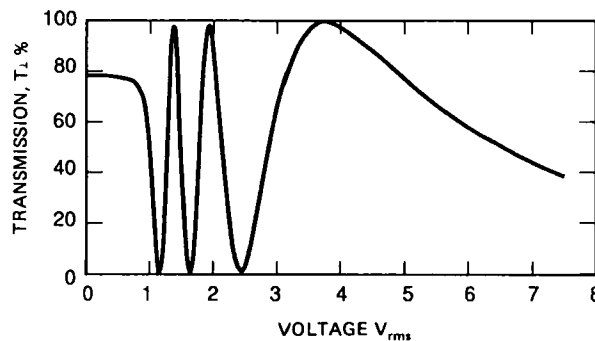


Figure 1. Voltage dependent transmission of an $8.6 \mu\text{m}$, parallel-aligned E-44 LC cell under crossed polarizers. The LC director is oriented at 45° to the axis of the polarizer. The applied a.c. voltage has sinusoidal waveform, with frequency = 10 kHz . The operation temperature $T \cong 22^\circ\text{C}$ and $\lambda = 632.8 \text{ nm}$. The total phase retardation of the LC cell is 6.73π .

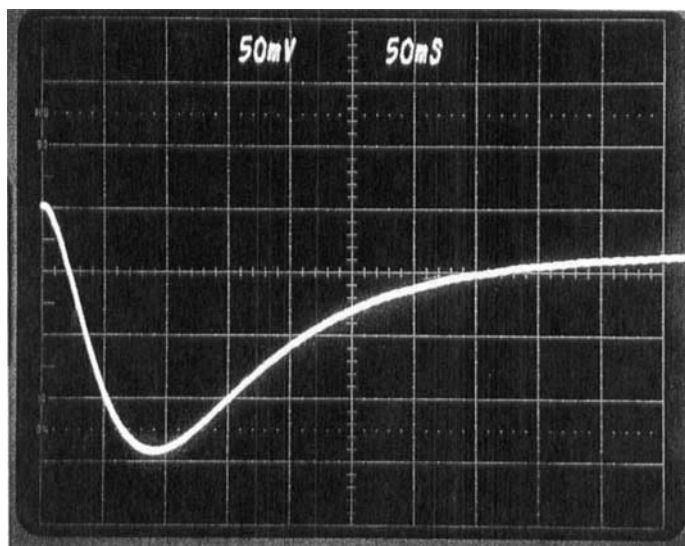


Figure 2. Transient intensity decay time of the LC cell under study. The bias voltage $V_1 = 1.35 V_{rms}$. At $t = 0$, the voltage is turned off instantaneously. From peak to valley, the phase change is 1π . The total phase change from V_1 to $V = 0$ is 1.73π . The associated transient phase change can be calculated using equation (8). Vertical scales represent light intensity. Time = 50 ms/div.

to be 0.247 for $\lambda = 632.8$ nm. A small voltage (V_1 , corresponding to the first transmission maximum shown in figure 1) which is not too far from the threshold voltage (V_{th}) is applied to the cell such that the phase retardation of the cell is reduced to 5π . When the voltage is removed instantaneously, the optical transmission should initially drop and then climb up as shown in figure 1. From V_1 to $V = 0$, the net phase change is $\delta_0 = 1.73\pi$. The time dependent relaxation curve is shown in figure 2. Although figure 2 shows the time dependent intensity change ($I(t)$) of the LC cell under crossed polarizers, its associated phase change ($\delta(t)$) can be calculated using the following relationship:

$$I(t) = I_0 \sin^2 \{[\Delta_{tot} - \delta(t)]/2\}, \quad (8)$$

where I_0 stands for the maximum intensity change. Once $\delta(t)$ is obtained, $\ln[\delta_0/\delta(t)]$ as a function of time can be calculated and plotted. Results are shown in figure 3. Indeed, a linear relationship as predicted by equation (7) is found. From the slope measurement (slope = $2/\tau_0$), τ_0 is found to be 215 ms. Knowing that $d = 8.6 \mu\text{m}$, γ_1/K_{11} is calculated to be $28.7 \text{ ms}/\mu\text{m}^2$ at $T = 22^\circ\text{C}$. This result is in good agreement with that reported in [14] where the transient intensity response as described in [12] was used for measurement. Unlike the method developed in [12] which is restricted to some special phase conditions, the present technique is more general in terms of application; it can be used at any LC layer thickness, temperature, and wavelength. The only constraint of the present technique is that it has to be used under the small signal excitation regime in order to obtain an accurate result.

2.2. Order parameter

Temperature dependent Δn and γ_1/K_{11} were measured for each LC studied. Temperature dependent birefringence of a LC is mainly determined by the orientational

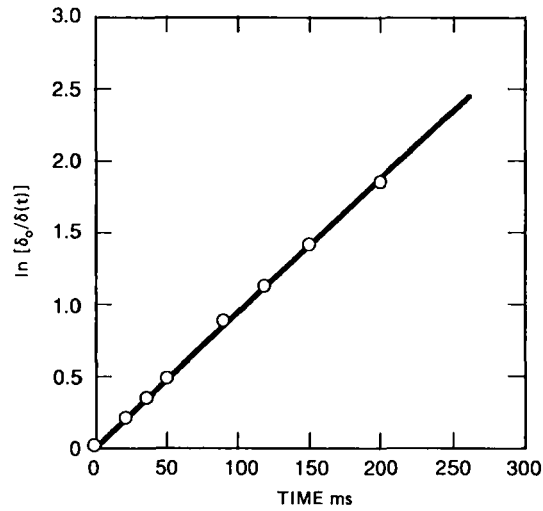


Figure 3. Transient phase decay time as calculated from figure 2. From the slope measurement, the free relaxation time of the $8.6\ \mu\text{m}$ E-44 cell is found to be 215 ms. From this decay time, γ_1/K_{11} is calculated to be $28.7\ \text{ms}/\mu\text{m}^2$ at $T = 22^\circ\text{C}$.

order parameter S (the density variation is small and is neglected) [15, 16]:

$$\Delta n(\lambda, T) = \Delta n_o(\lambda)S(T), \quad (9)$$

where $\Delta n_o(\lambda)$ represents the birefringence at λ while assuming $S = 1$, i.e. the completely ordered state. Moreover, the temperature-dependent order parameter can be approximated by [17]:

$$S = (1 - T/T_{\text{NI}})^\beta, \quad (10)$$

where T_{NI} represents the nematic-isotropic phase transition temperature (in degrees K) and β is a material constant. Equation (10) holds pretty well in a large portion of the nematic range, except in the vicinity of the phase transition temperature where the first order phase transition implies a discontinuity in S —but equation (10) shows no such feature. Outside this narrow transition region ($T_{\text{NI}} - T < 1^\circ\text{C}$), equation (10) fits experimental results well. Thus, from temperature dependent birefringence measurement, parameters Δn_o and β can be obtained by computer fitting to the experimental results. Once β is known, S can be calculated at any temperature (T) or reduced temperature ($T_{\text{R}} = T/T_{\text{NI}}$). This calculated S agrees very well with that measured by the infrared absorption anisotropy method. [18].

2.3. Elastic constant

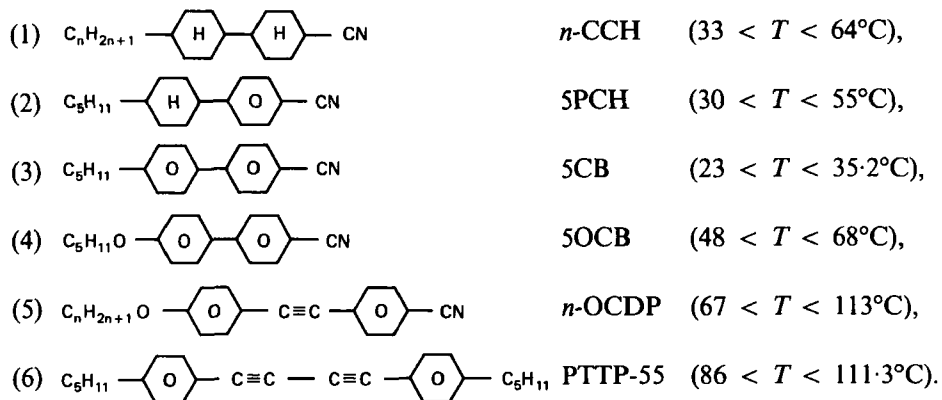
The temperature dependent splay elastic constant (K_{11}) has been studied extensively. Both theory [19, 20] and experimental results [21] show that

$$K_{11} \propto S^2. \quad (11)$$

Our experimental results also support this relationship, as will be shown later. Combining our results on γ_1/K_{11} and knowing that K_{11} is proportional to S^2 , temperature dependent γ_1 is obtained. These experimental results are then used to test existing theories.

3. Experimental results

Six nematic compounds with different conjugation lengths, including two binary mixtures for the purpose of widening their nematic range, were used for this study. They are



The n -CCH and n -OCDP [22] are binary mixtures; they consist of 50 per cent 2-CCH and 50 per cent 4-CCH, and 25 per cent 2-OCDP and 75 per cent 4-OCDP, respectively. The results of PTPP-55 were taken from [23].

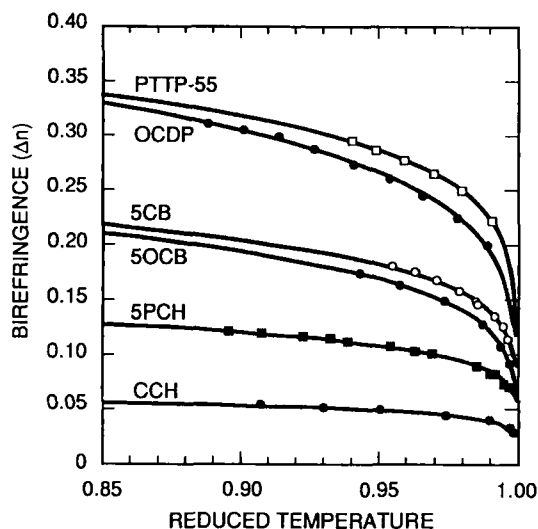


Figure 4. Reduced temperature dependent birefringence of six LC compounds studied. The wavelength used for measurements is $\lambda = 632.8$ nm. Solid lines represent fittings with experimental results using $\Delta n = \Delta n_0(1 - T_R)^\beta$. The parameters Δn_0 and β used for computer fittings are listed in table 1.

Temperature dependent birefringence of these LCs was measured at $\lambda = 632.8$ nm. Results are shown in figure 4. Solid lines in figure 4 represent fitting of experimental results with equation (9) and (10). Parameters (Δn_0 and β) used for fittings are listed in table 1. From the obtained β , we can calculate the order parameter for each LC at any temperature of interest.

Table 1. Parameters used in $\Delta n = \Delta n_0(1 - T_R)^\beta$ for fitting the experimental results shown in figure 4. T_R stands for the reduced temperature, i.e. $T_R = T/T_{NI}$. The standard deviation of these fittings is about 1×10^{-3} .

	Δn_0	β
<i>n</i> -CCH	0.0764	0.1529
5PCH	0.1734	0.1573
5CB	0.3000	0.1650
5OCB	0.3117	0.2043
<i>n</i> -OCDP	0.4792	0.1951
PTTP-55	0.4545	0.1531

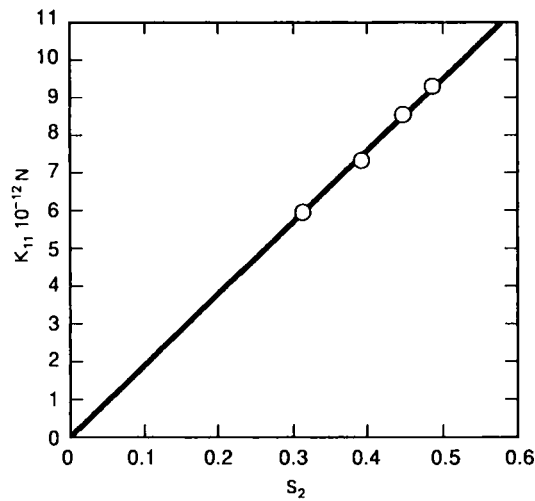


Figure 5. Validation of $K_{11} \sim S^2$. The LC used is 5PCH. The order parameter is calculated from equation (10) with the β listed in table 1. The experimental data on K_{11} are taken from [24].

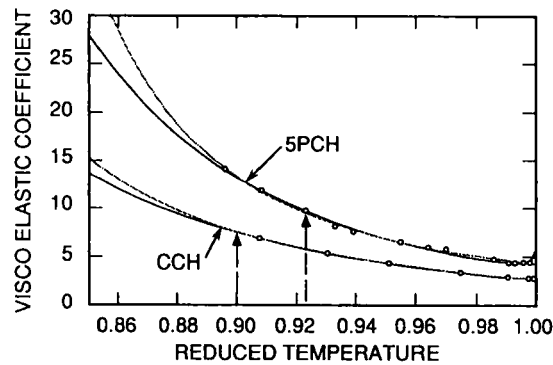


Figure 6. Reduced temperature dependent viscoelastic coefficient of CCH and 5PCH. Open circles are experimental results. The solid and dashed lines represent fittings using Models 7 and 5, respectively, as listed in equation (4). Parameters used for fittings are listed in table 3 and 4 for Models 5 and 7, respectively. The vertical bars indicate the melting points of the LCs.

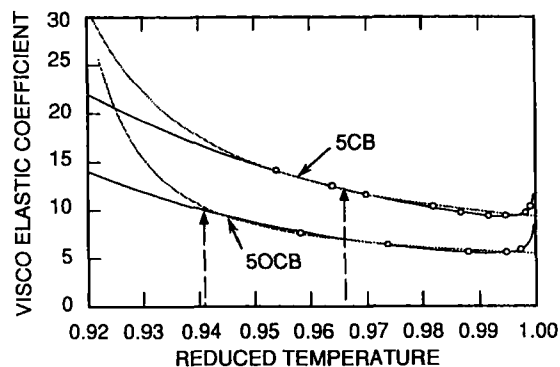


Figure 7. Reduced temperature dependent viscoelastic coefficient of 5CB and 5OCB. Open circles are experimental results. The solid and dashed lines represent fittings using Models 7 and 5, respectively as listed in equation (4). Parameters used for fittings are listed in tables 3 and 4 for Models 5 and 7, respectively. The vertical bars indicate the melting points of the LCs.

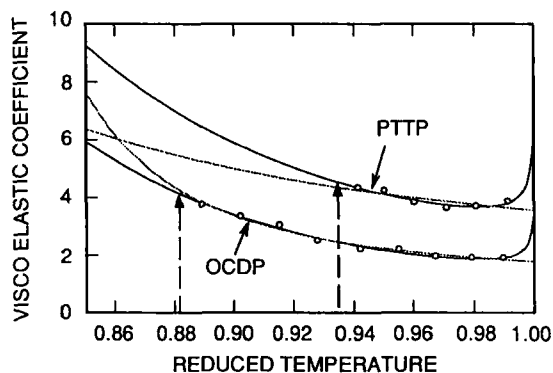


Figure 8. Reduced temperature dependent viscoelastic coefficient of PTTP and OCDP. Open circles are experimental results. The solid and dashed lines represent fittings using Models 7 and 5, respectively as listed in equation (4). Parameters used for fittings are listed in tables 3 and 4 for Models 5 and 7, respectively. The vertical bars indicate the melting points of the LCs.

Using the order parameter we obtained for 5PCH and the elastic constant measured by the E. Merck group, [24] we validate the relationship $K_{11} \sim S^2$, as shown in figure 5. More evidence on this relationship was reported in [21] for various molecular structures. Thus, the temperature dependence of γ_1 , as we deduced from γ_1/K_{11} measurements and equation (11), is reliable.

Experimental results on the reduced temperature dependent viscoelastic coefficient (γ_1/K_{11}) of the six LCs under study are shown as the open circles in figures 6, 7, and 8. The solid and dashed lines represent the fitting of Models 7 and 5, respectively, as will be discussed later. The vertical lines in these figures stand for the melting points of these six LCs. Some data were taken under super cooled conditions so that the measurement temperatures could be extended a few degrees below the specified melting point.

4. Comparison

The obtained experimental results of γ_1/K_{11} , as shown in figures 6–8 are then used to compare with the seven models as listed in equation (4). The relationship of $K_{11} \sim S^2$ is used for all cases. Although quantitative results (42 fittings) for each sample and each model are available, it will be tedious for us to display all these 42 figures. We only summarize our qualitative results in table 2. Results are divided into five categories: excellent, satisfactory, fair, unsatisfactory, and failure based on the standard deviation of computer fittings. As we can see from table 2, Model 1 (Arrhenius's law) and Model 4 (Martins and Diogo's theory) always give unsatisfactory fittings to all the samples studied. Model 2 (used by DeJeu) gives excellent fittings on highly conjugated LC molecules, but not so good for the totally saturated molecules. Model 3 (Hess equation) and Model 6 (Diogo and Martin's free volume

Table 2. Qualitative comparison of the computer fittings of six LCs with seven models as described in equation (4). A, excellent; B, satisfactory; C, fair; D, unsatisfactory; and F, failure.

	<i>n</i> -CCH	5PCH	5CB	5OCB	<i>n</i> -OCDP	PTTP-55
Model 1	F	D	F	F	C	B
Model 2	D	B	C	B	A	A
Model 3	A	B	B	C	B	B
Model 4	D	D	D	D	C	C
Model 5	A	A	B	B	B	B
Model 6	B	B	B	C	B	B
Model 7	A	A	A	A	A	A

Table 3. Parameters used in Model 5 for fitting the experimental results as shown in figures 6–8. Here, $\gamma_1/K_{11} = \alpha'_2 \exp[E/k(T - T_0)]$; α'_2 is a new proportionality constant.

	$\alpha'_2/$ ms/ μm^2	$E/$ meV	$T_0/$ K
<i>n</i> -CCH	0.06	56.8	167.3
5PCH	0.29	26.5	215.2
5CB	5.0	2.2	269.8
5OCB	3.8	1.18	307.3
<i>n</i> -OCDP	0.65	8.11	289.6
PTTP-55	1.0	20.2	199.2

Table 4. Parameters used in Model 7 for fitting the experimental results as shown in figures 6–8. Here, $\gamma_1/K_{11} = (\alpha'_1 S^{-1} + \alpha'_2) \exp(E/kT)$; α'_1 and α'_2 are new proportionality constants.

	$\alpha'_1/$ ms/ μm^2	$\alpha'_2/$ ms/ μm^2	$E/$ meV
<i>n</i> -CCH	1.50×10^{-5}	2.96×10^{-4}	263.6
5PCH	6.79×10^{-6}	2.24×10^{-5}	329.3
5CB	9.45×10^{-6}	3.54×10^{-5}	317.7
5OCB	5.95×10^{-7}	1.18×10^{-6}	423.7
<i>n</i> -OCDP	4.47×10^{-5}	8.57×10^{-6}	319.2
PTTP-55	6.99×10^{-4}	0	258.6

theory) generally give satisfactory fittings except for alkoxy-cyano-biphenyl. It should be pointed out that Models 1–4 use only two adjustable parameters. Thus, Model 3 is considered as a good model. Models 5 and 7 give very good fittings on all six samples regardless of their difference in conjugation length. These two fittings are shown in figures 6–8 as mentioned earlier. The parameters used for these fittings are listed in tables 3 and 4 for models 5 and 7, respectively.

Although both Model 5 and Model 7 fit experimental results well in the nematic range, there are still two different features between them. The first is that Model 5 shows a very small activation energy due to the presence of a ‘freezing’ temperature T_0 . As T approaches T_0 , the rotational viscosity starts to diverge. This diverging phenomenon is less pronounced in Model 7. This is because $T_0 = 0$ in Model 7. Although Model 5 predicts a more pronounced divergence in γ_1 , this prediction is difficult to verify experimentally because the available measurement temperature (T) is always much higher than T_0 . In the nematic range of a LC, the difference between these two models is rather small. The second difference appears in the vicinity of T_{NI} . In some LC substances with long conjugation length, Model 7 shows a slowing-down phenomenon (i.e. γ_1/K_{11} bounces back) as T approaches T_{NI} . However, Model 5 predicts a monotonous decrease in γ_1/K_{11} . As pointed out by the authors in [6], their data fit Model 5 very well if the data points near T_{NI} are omitted. This observation basically agrees with ours although the two measurement techniques are totally different.

The slowing-down phenomenon in γ_1/K_{11} (but not in γ_1 alone) is not difficult to understand. For simplicity, let us take a simple form of γ_1 as

$$\gamma_1 \sim S^x \exp(E/kT). \quad (12)$$

Combining equations (10), (11) and (12), we can write γ_1/K_{11} as

$$\gamma_1/K_{11} = \alpha(1 - T/T_{NI})^{(x-2)\beta} \exp(E/kT), \quad (13)$$

where α is a proportionality constant. To determine whether equation (13) has a minimum which occurs at a temperature T_{min} , we set $\partial(\gamma_1/K_{11})/\partial T = 0$ and lead to

$$(2 - x)\beta = \frac{E}{kT_{min}} \left(\frac{T_{NI}}{T_{min}} - 1 \right). \quad (14)$$

Equation (14) shows that if $x = 2$, then the minimum of γ_1/K_{11} appears at $T_{min} = T_{NI}$. That is to say, in the nematic range, γ_1/K_{11} decreases monotonously with increasing temperature. This is exactly what happens in Model 5 where $x = 2$ so that no minimum for γ_1/K_{11} appears within the nematic range. On the other hand, if $x = 1$, a minimum of γ_1/K_{11} exists and occurs at [22]

$$\begin{aligned} T_{min} &= (E/2\beta k)[(1 + 4\beta k T_{NI}/E)^{1/2} - 1] \\ &\approx T_{NI}(1 - \beta k T_{NI}/E). \end{aligned} \quad (15)$$

Since $\beta k T_{NI}$ is usually far less than E , T_{min} is very close to T_{NI} . This is what we observe in the experimental data shown in figures 7 and 8 in which the slowing-down phenomenon is more manifest. However, for 5PCH and CCH as shown in figure 6, the slowing-down phenomenon is not observed.

After a more careful examination of the parameters listed in table 4 for Model 7, we find that for highly saturated LC molecules, $\alpha_1 \ll \alpha_2$. That means the primary leading term in $f(S)$ is the S^2 term; the contribution of the first order term exists but

is insignificant. As the conjugation length increases, the situation is reversed. The role of the first order term is increasing and the second order term decreasing. For a highly conjugated LC such as PTPP, the S^2 term vanishes completely.

Model 7 gives excellent fittings to all experimental results. However, its physical origins remain to be explored in greater detail. In particular, the conjugational effect seems to imply that the intermolecular interactions among conjugated LC molecules are quite different from those for saturated LC molecules.

A similar conjugational effect on γ_1 has been reported by Belyaev *et al.* [11] In their studies, they found the temperature dependent γ_1 is represented by

$$\gamma_1 = a_1 S \exp(E_1/kT) + a_2 S^2 \exp(E_2/kT), \quad (16)$$

where a_1 and a_2 are proportionality constants, E_1 and E_2 are activation energy. In general, this equation contains four unknowns, and is unlikely to give a meaningful fitting of experimental results. Nevertheless, in two extreme cases the authors deduced that $a_1 = 0$ for a LC containing a fragment with saturated bonds (such as cyclohexane) and $a_2 = 0$ for a long conjugated LC molecule (such as alkoxy-cyanobiphenyl). Despite some differences on the definition of 'long' conjugation, Model 7 agrees with equation (16) for the two extreme cases—(1) completely saturated bonds, and (2) highly conjugated molecular chains. With regard to the intermediate conjugation, Model 7 is recommended to be used for describing γ_1 although its physical origins remain to be investigated.

5. Discussion

The LCs we used for viscosity measurements all exhibit a simple phase transition sequence, that is from crystal to nematic to isotropic phase, as temperature increases; no smectic A phase is present. For LCs possessing both smectic A and nematic phases, the short range smectic A ordering [25] makes an important contribution to the observed rotational viscosity at the vicinity near the nematic-smectic-A transition temperature (T_{NA}). Under this circumstance, γ_1 in the nematic phase consists of two parts [26]:

$$\gamma_1 = \gamma_1^0 + C(T/T_{NA} - 1)^{-v/2} \quad (17)$$

where γ_1^0 is the intrinsic rotational viscosity, C is the proportionality constant, and v is an exponent. The second term in equation (17) originates from the pretransitional effect owing to the short range smectic A ordering. From equation (17), γ_1 may increase rapidly as T approaches T_{NA} . This phenomenon has been observed experimentally [26]. Through a series of skilful measurements, Huang *et al.* [26] and Jähnig and Brochard [27] have determined that $v/2 = 0.37 \pm 0.05$ for the LC compound they studied, *N-p*-cyanobenzylidene-*p*-octyloxyaniline (CBOOA).

For a LC possessing both smectic A and nematic phases, such as 8CB and 8OCB, the equation (17) has to be used to fit experimental data. In order to limit the fitting parameters to less than three, we can only select the simplest form (two parameters) of γ_1^0 as shown in equation (2); for instance, $\gamma_1^0 = \alpha_0 \exp(E/kT)$ or $\gamma_1^0 = \alpha_2 S^2 \exp(E/kT)$. For any more complicated γ_1 , fitting of experimental results using equation (17) would involve at least four parameters which may lead to ambiguous interpretation of the obtained results.

All the LCs we studied (such as 5CB and 5OCB) do not have a smectic A phase. However, due to the fact that some higher homologs of cyano-biphenyl compounds (such as 8CB and 8OCB) do have a smectic A phase, speculation on the existence of

short range smectic A ordering, as well as its impact on our results, need to be clarified. To take this pretransitional effect into account we can, in principle assume that these LCs exhibit a virtual T_{NA} and use equation (17) to fit experimental results. Generally speaking, these fittings are impossible because there are at least four unknowns (α_0 , E , C , and T_{NA}). Nevertheless, by careful examination of our experimental data shown in figures 6–8, we find no abnormal increase in γ_1 as temperature is lowered throughout the whole nematic range. This observation implies that either the virtual T_{NA} is far below the melting point of each LC or the proportionality constant is too small to make a noticeable contribution. It is hard to find a physical justification for a too-low virtual T_{NA} . Therefore, we believe that the short-range smectic A ordering, if it exists at all in the samples we studied, would not make an important contribution to our analysis and can be ignored.

6. Conclusion

We have developed a simple and convenient electro-optical method for measuring the viscoelastic coefficient of a LC. With the validation of $K_{11} \sim S^2$, we can deduce the functional form of rotational viscosity. Results of six LCs with different conjugation lengths are used to compare with seven most frequently used models. Although two models give excellent fits to all experimental results, their physical origins remain to be investigated.

References

- [1] IMURA, H., and OKANO, K., 1972, *Jap J. appl. Phys.* **11**, 1440.
- [2] HESS, S., 1975, *Z. Naturf. A*, **30**, 1224.
- [3] MARTINS, A. F., and DIOGO, A. C., 1975, *Portgal. Phys.*, **9**, 1.
- [4] DIOGO, A. C., and MARTINS, A. F., 1981, *Molec. Crystals liq. Crystals*, **66**, 133.
- [5] OSIPOV, M. A., and TERENTJEV, E. M., 1989, *Physics Lett. A*, **134**, 301.
- [6] For a brief review, see KNEPPE, H., SCHNEIDER, F., and SHARMA, N. K., 1982, *J. chem. Phys.*, **77**, 3203.
- [7] DEJEU, W. H., 1981, *Molec. Crystals liq. Crystals*, **63**, 83.
- [8] HELFRICH, W., 1972, *J. chem. Phys.*, **56**, 3187.
- [9] SIEDLER, L. T. S., HYDE, A. J., PETHRICK, R. A., and LESLIE, F. M., 1983, *Molec. Crystals liq. Crystals*, **90**, 255.
- [10] LEENHOUTS, F., 1985, *J. appl. Phys.*, **58**, 2180.
- [11] BELYAEV, V. V., IVANOV, S. A., and GREBENKIN, M. F., 1986, *Sov. Phys. Crystallogr.*, **30**, 674.
- [12] WU, S. T., 1986, *J. appl. Phys.*, **60**, 1836.
- [13] JACKMAN, E., and RAYNES, E. P., 1972, *Phys. Lett. A*, **39**, 69.
- [14] WU, S. T., LACKNER, A. M., and EFRON, U., 1987, *Appl. Optics*, **26**, 3441.
- [15] WU, S. T., 1986, *Phys. Rev. A*, **33**, 1270.
- [16] AVER'YANOV, E. M., and SHABANOV, V. F., 1978, *Sov. Phys. Crystallogr.*, **23**, 177.
- [17] HALLER, I., 1975, *Prog. Solid State Chem.*, **10**, 103.
- [18] WU, S. T., 1987, *Appl. Optics*, **26**, 3434.
- [19] SAUPE, A., 1960, *Z. Naturf. A*, **15**, 810.
- [20] GRULER, H., 1975, *Z. Naturf. A*, **30**, 230.
- [21] BRADSHAW, M. J., McDONNELL, D. G., and RAYNES, E. P., 1981, *Molec. Crystals liq. Crystals*, **70**, 289.
- [22] WU, S. T., and NGUYEN, H. T., 1989, *J. appl. Phys.*, **66**, 2332.
- [23] WU, S. T., FINKENZELLER, U., and REIFFENRATH, V., 1989, *J. appl. Phys.* **65**, 4372.
- [24] FINKENZELLER, U., GEELHAAR, T., WEBER, G., and POHL, L., 1989, *Liq. Crystals*, **5**, 313.
- [25] McMILLAN, W. L., 1974, *Phys. Rev. A*, **9**, 1720.
- [26] HUANG, C. C., PINDAK, R. S., FLANDERS, P. J., and HO, J. T., 1974, *Phys. Rev. Lett.*, **33**, 400.
- [27] JÄHNIG, F., and BROCHARD, F., 1974, *J. Phys., Paris*, **35**, 301.