Determination of viscoelastic coefficients from the optical transmission of a planar liquid crystal cell with low-frequency modulated voltage

H. Schmiedel, R. Stannarius, and M. Grigutsch
Fachbereich Physik der Universität Leipzig, 04103 Leipzig, Germany

R. Hirning, J. Stelzer, and H.-R. Trebin
Institut für Theoretische und Angewandte Physik, Universität Stuttgart, Institut fur Theoretische und Angewandte Physik, 70550 Stuttgart, Germany

(Received 17 May 1993; accepted for publication 19 July 1993)

The viscoelastic response of the nematic director field to low-frequency modulations of the driving voltage was studied by means of optical transmission measurements. An external ac voltage above the critical field U_c was weakly amplitude modulated with frequencies in the range of 1 to 100 Hz. The viscosity coefficients α_1, γ_1, γ_2, and η_b influence the time dependence of the director field. They were determined by fitting the phase and amplitude of theoretically calculated optical transmission curves to measured data.

I. INTRODUCTION

The dynamical behavior of liquid crystals is described by the Leslie–Ericksen equations. In three-dimensional geometry, there are six Leslie viscosity coefficients, five of them being independent. In a one-dimensional geometry, the motion depends on four viscosities only. The examination of the electro-optical switching of thin planar cells near the Fréedericksz threshold U_c provides the rotational viscosity γ_1. The other viscosities cannot be obtained in such an easy way. There are, however, alternative experimental methods that allow a more or less direct determination, too.[1–6]

Our intention has been to find a method to measure all four viscosity coefficients in a simple experimental setup. We modified an existing device for measuring elastic constants[7] by changing the driving ac voltage from a constant effective value to a weakly modulated voltage, and we performed time dependent measurements.

If the voltage U of a planar nematic cell is changed sufficiently slowly, the director field in the cell follows the changes of U adiabatically in a state of stationary equilibrium (free energy minimum). We denote this case as "quasistatic." Thus, one can determine the elastic constants K_{11} and K_{33}. If the amplitude of a voltage $U > U_c$ is modulated with a period comparable to the characteristic switching time of the cell, the director response is delayed with respect to the changes of the electric field and the amplitude of the director reorientation decreases. This fact is reflected by a phase shift between the optical transmission and the electrical input, and by a decrease of the modulation amplitude of the transmission function. Normally, nematic LC displays are driven by electric fields of frequencies within the order of kHz. At such frequencies, the director field in the display cell experiences the effective value of the applied voltage only, because the nematic is too viscous to follow the rapidly alternating (e.g., sinusoidal) electric field.

The frequency dependence of amplitude and phase of the optical transmission curve provides information on all four viscosity coefficients mentioned above. If U is switched on or off between zero and a voltage slightly above U_c, an independent method for the determination of γ_1 is applicable to the same system.

II. EXPERIMENTAL SETUP

The typical electro-optical characteristic of a planar cell is shown in Fig. 1. The diagram was recorded quasistatically. With increasing effective voltage, the director field is deformed gradually from planar to almost homeotropic orientation. The optical transmission of the cell with crossed polarizers in 45° orientation to the surface alignment is determined by the interference of the ordinary wave subject to the index of refraction n_o and the extraordinary wave which experiences an effective index n_{eff}. The latter decreases with increasing director deformation from n_e to n_o, and the optical transmission passes through several interference maxima and minima.

The cells were illuminated with monochromatic light, $\lambda = 632.8$ nm, by a laser source at normal incidence. The integral transmission intensity over an active spot of approximately 1 mm^2 was measured by a photomultiplier and was recorded digitally with a homebuilt setup. Finally, data were transmitted to a PC for processing and storage.

The sample cells were made from ITO-coated glass plates with an orienting layer of 60° obliquely evaporated SiO. This surface preparation provides planar alignment of the director at the glass with strong anchoring. The cells were filled with the nematic mixture ZLI 2293 (Merck), whose clearing point is between 81 and 85 °C. Cells of thicknesses between 10 and 40 μm have been prepared with different spacer foils. The cell thickness has been determined from interference patterns by infrared transmission spectroscopy of the empty cells.

For the study of the dynamics of the liquid crystal, we chose an offset voltage U_0 so that the static transmission was approximately in the middle of one of the slopes of the interference curve. We modulated the voltage at the electrodes with a low frequency f_m (1...100 Hz) and an amplitude U_m (Fig. 1):

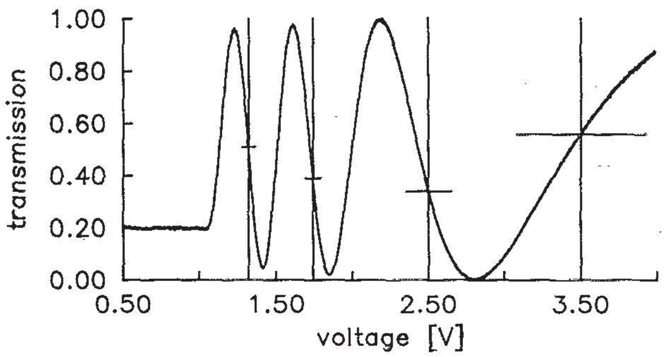

FIG. 1. Experimental static transmission of a planar cell as function of applied effective voltage, crossed polarizers in 45° position. Vertical bars: offset voltages U_0 chosen in the modulation experiments. Horizontal bars: modulation amplitudes U_m. Nematic substance: ZLI 2293 (Merck), $T_{red}=0.906$ (51.5 °C).

$$U_{eff}(t)=U_0+U_m\cos(2\pi f_m t).$$

The modulation amplitude was small enough to provoke a linear response of the optical transmission to changes in U. However, our calculations provide an exact solution of the Leslie–Ericksen equations, and the optical characteristics are computed by the 4×4 matrix formalism. Therefore, there are no limiting assumptions in the theoretical fitting procedure, and linearity of the transmission response function is not required. In principle, any modulation offset and amplitude could be applied, but choosing a point of linear slope of the static curve and small modulation amplitudes makes the fitting procedure much easier.

In practice, we used a constant carrier frequency of 1 kHz in all experiments. Only its effective value was modulated. This frequency is fast enough to avoid dc effects in the sample. The director is sensitive to the effective value of the carrier. Furthermore, the dielectric anisotropy $\Delta\epsilon$ is slightly frequency dependent. With a constant carrier frequency we can use the value of $\Delta\epsilon$ for 1 kHz in all experiments.

Due to the viscosity of liquid crystals, the optical transmission for a modulated external electric field follows the static characteristics of Fig. 1 only at very low frequencies. With increasing f_m, it deviates from the quasistatic curve, but after a short time the transmission versus voltage becomes a stationary Lissajous figure (Fig. 2). This

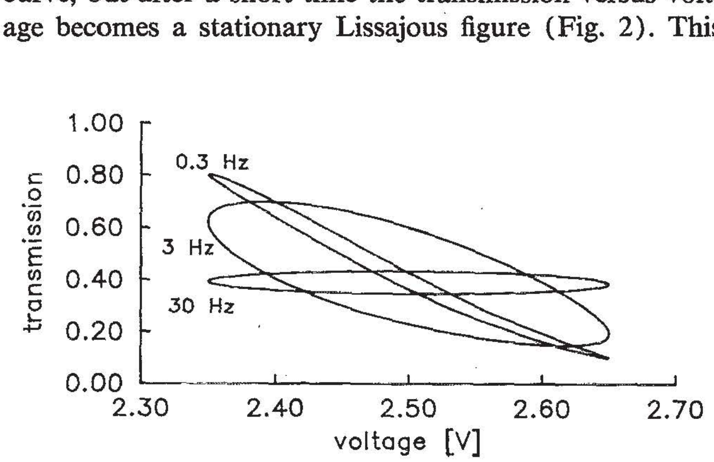

FIG. 2. Transmission vs voltage for different modulation frequencies. Nematic substance: ZLI 2293 (Merck), $T_{red}=0.906$ (51.5 °C).

curve was recorded with a device normally used for measuring elastic constants.[7] In each experiment, we have recorded 16 cycles of the stationary figures and averaged them to one cycle. Subsequent runs with the same offset and modulation resulted in reproducible and stable Lissajous figures.

III. THEORY

Take a nematic layer of thickness d with the layer normal coinciding with the z axis of a Cartesian coordinate system. At both surfaces of the layer, the director is anchored parallel to the x axis. Thus the azimuthal angle is constant, and the director can be described by a tilt angle $\theta(z,t)$ only. θ is measured with respect to the x axis. The motion of the director is coupled to a macroscopic mass flux v in the x direction (backflow[8]).

The evolution of θ and v under an applied voltage $U_{eff}(t)$ is described by a system of coupled partial differential equations, the Leslie–Ericksen equations:[9,10]

$$\sigma^{\langle zx\rangle}=f_1(\theta)v_z-f_2(\theta)\dot{\theta}, \tag{1}$$

$$\gamma_1\dot{\theta}=f_3(\theta)\theta_{zz}+\tfrac{1}{2}f_3'(\theta)\theta_z^2+f_4(\theta)E^2+f_2(\theta)v_z, \tag{2}$$

with

$$f_1(\theta)=\tfrac{1}{4}\alpha_1\sin^2 2\theta+\eta_b-\gamma_2\sin^2\theta,$$

$$f_2(\theta)=\gamma_2\sin^2\theta-\tfrac{1}{2}(\gamma_1+\gamma_2),$$

$$f_3(\theta)=K_{11}\cos^2\theta+K_{33}\sin^2\theta,\ f_3'(\theta)=\frac{df_3(\theta)}{d\theta},$$

$$f_4(\theta)=\tfrac{1}{2}\epsilon_0(\epsilon_\parallel-\epsilon_\perp)\sin 2\theta,$$

$$\dot{\theta}=\frac{\partial\theta}{\partial t},\quad \theta_z=\frac{\partial\theta}{\partial z},\quad \theta_{zz}=\frac{\partial^2\theta}{\partial z^2},\quad v_z=\frac{\partial v}{\partial z}.$$

$\sigma^{\langle zx\rangle}$ is the zx component of the nematic strain tensor; E is the z component of the electric field:

$$E(z,t)=\frac{U_{eff}(t)}{(\epsilon_\parallel\cos^2\theta+\epsilon_\perp\sin^2\theta)}\times\left(\int_0^d\frac{dz}{\epsilon_\parallel\cos^2\theta+\epsilon_\perp\sin^2\theta}\right)^{-1}.$$

Finally, K_{11} and K_{33} are the Frank elastic constants for splay and bend deformation, respectively. γ_1 and γ_2 are the rotational viscosities, and η_b is the shear viscosity. The viscosities γ_1, γ_2 and η_b can be expressed by the Leslie coefficients $\alpha_1\ldots\alpha_6$:

$$\gamma_1=\alpha_3-\alpha_2,\quad \gamma_2=\alpha_3+\alpha_2,\quad \eta_b=\tfrac{1}{2}(\alpha_4+\alpha_3+\alpha_6). \tag{3}$$

Following the work of van Doorn,[11] in Eqs. (1) and (2) we neglected the inertial terms containing second order time derivatives of θ.

The Eqs. (1) and (2) are subject to the obvious boundary conditions for strong anchoring:

$$\theta(z=0,t)=\theta(z=d,t)=0\quad\text{and}$$

$$v(z=0,t)=v(z=d,t)=0.$$

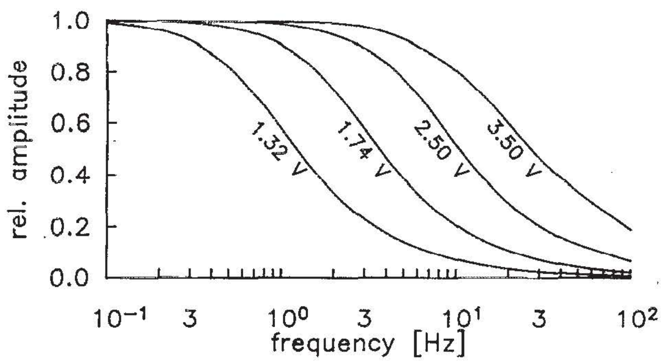

FIG. 3. Relative amplitudes of the response for the offset voltages given in Fig. 1. The amplitude for frequency 0 is used as reference.

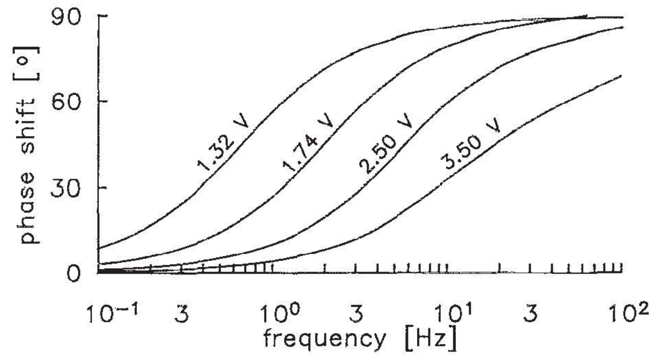

FIG. 4. Phase shift between the response and the driving voltage for the offset voltages given in Fig. 1.

By eliminating v_z one arrives at the equation:

$$\gamma_{\text{eff}}\dot{\theta}=f_3\theta_{zz}+\frac{1}{2}f_3'\theta_z^2+f_4E^2+\sigma^{(zx)}\frac{f_2}{f_1},\tag{4}$$

which is similar to Eq. (2) and thus can be interpreted in terms of an effective rotational viscosity γ_{eff}, where

$$\gamma_{\text{eff}}(\theta)=\gamma_1-\frac{f_2^2}{f_1}.\tag{5}$$

After solving the Leslie–Ericksen equations numerically, the theoretical transmission curve for monochromatic light passing through the layer between crossed polarizers is obtained as a function of viscosities and elastic constants.

Starting from an arbitrary director deformation, the solution of the above system of differential equations for a low-frequency modulated external electric field leads to a stationary cyclic behavior of the director field. The cyclic optical transmission function corresponding to the director field is determined by application of geometrical optics.

$$I=I_0\sin^2\left(\pi(n_{\text{eff}}-n_o)\frac{d}{\lambda}\right)\tag{6}$$

is the transmission function which depends on the director field via the effective index of refraction

$$n_{\text{eff}}=\int_0^d\frac{n_e\,n_o}{\sqrt{[n_o^2\cos^2(\theta)+n_e^2\sin^2(\theta)]}}\,dz.$$

In the case of normal incidence of light without any twist in the director field Eq. (6) above, coming from pure geometrical optics, and the 4×4-matrix method we used in the calculation yield the same results.

The response of the liquid crystal to a low-frequency modulated voltage (Figs. 3 and 4) can be used to determine visco-elastic material parameters by fitting the simulated transmission to the measured one for a set of experiments. Keeping the temperature constant, experiments can be performed at different slopes of the transmission curve (see Fig. 1). At offset voltages U_0 near the Fréedericksz threshold U_c, a good approximation to γ_{eff} is given by η_{splay}, where

$$\eta_{\text{splay}}=\gamma_{\text{eff}}(\theta=0)=\gamma_1-\frac{\alpha_3^2}{\eta_b}.$$

Because for elongated molecules $|\alpha_3|\ll|\alpha_2|$ and hence $\gamma_{\text{eff}}\approx\gamma_1$, we expect good values for γ_1. At higher offset voltages ($U_0\gg U_c$), the director is more aligned with the electric field than for low voltages. Thus

$$\eta_{\text{bend}}=\gamma_{\text{eff}}\left(\theta=\frac{\pi}{2}\right)=\gamma_1-\frac{\alpha_2^2}{\eta_b-\gamma_2}$$

is a good approximation to γ_{eff} and we expect good values for γ_2, η_b and α_1, too.

At each slope of the transmission versus voltage curve, i.e., at each offset voltage, a set of experiments was performed with different modulation frequencies, starting with very slow modulations where the director follows the field changes immediately, up to high modulation frequencies where the amplitude modulation of the optical transmission has decayed to zero. For all these measurements at constant temperature, one set of parameters γ_1, γ_2, α_1, and η_b was found that fits the experimental curves. This is the advantage of the method over a simple ON or OFF switching of the cell, where in principle all these parameters are involved, too, but—even by varying the voltages of the switching processes—it is difficult to select information about the different viscosity parameters.

IV. RESULTS AND DISCUSSION

From the static transmission curve of the cell used (Fig. 1), the elastic constants K_{11} and K_{33} were determined

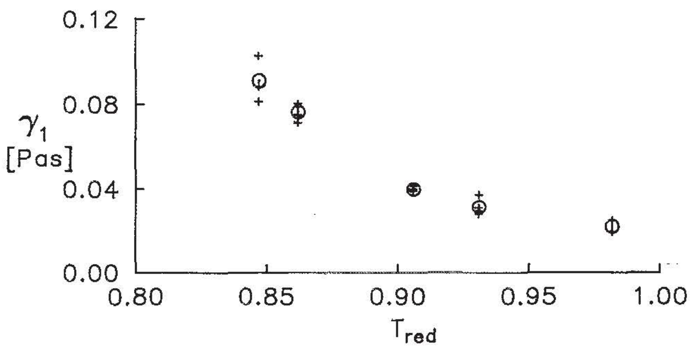

FIG. 5. Rotational viscosity γ_1. The crosses are values obtained by fitting the calculated transmission to the measured ones for several offset voltages. The circles give the average values.

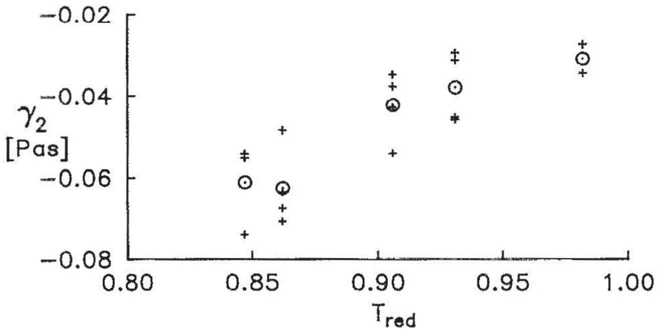

FIG. 6. Rotational viscosity γ_2. The crosses are values obtained by fitting the calculated transmission to the measured ones for several offset voltages. The circles give the average values.

with the method described in Ref. 7. The difference between the diffraction indices Δn is related to the transmission of light with wavelength λ at zero voltage, where the director pattern is homogeneous according to Eq. (6).

The initial intensity of the transmitted light I_0 corresponds to the maximum order of interference. As λ, n_e, and n_o are known with sufficient precision, Eq. (6) provides a control of the cell thickness measurement.

From the fit of the frequency dependence of the amplitudes and phases of the optical transmission curves, we have determined the viscosity coefficients in dynamic experiments. At each temperature, experimental Lissajous figures of the $I(U)$ dependence have been recorded at a set of frequencies f_m and for different offset voltages U_0. The modulation amplitudes U_m were kept small enough to stay in the linear slopes of the transmission curve. The vertical bars in Fig. 1 show the corresponding values of U_0 and U_m at one particular temperature. As we expected, the transition range from the low-frequency regime where the director follows the voltage function without delay and without loss in modulation amplitude to the high-frequency regime where the director averages the input modulation to an effective value shifts with increasing offset voltage. The transition frequency increases with higher offset voltage. This is reflected by Figs. 3 and 4 where the measured data are presented. The amplitudes decay from the value corresponding to the static curve down to zero, while the phase

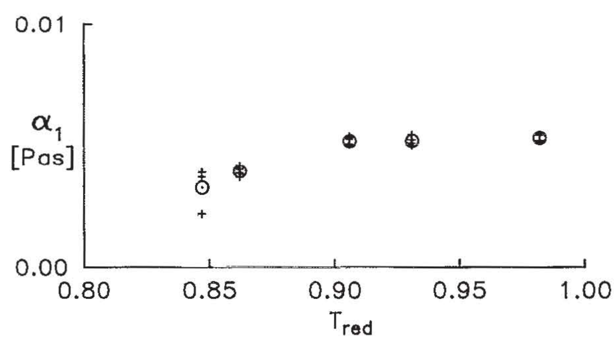

FIG. 7. Leslie viscosity coefficient α_1. The crosses are values obtained by fitting the calculated transmission to the measured ones for several offset voltages. The circles give the average values.

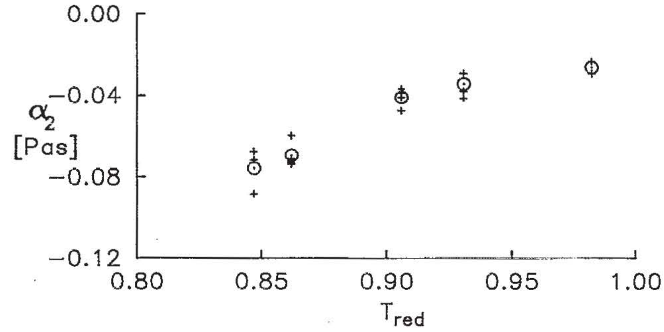

FIG. 8. Leslie viscosity coefficient α_2 calculated using Eq. (3). The crosses are values obtained by fitting the calculated transmission to the measured ones for several offset voltages. The circles give the average values.

shift of the Lissajous figure increases from zero to $\pi/2$. This is the behavior commonly known from a damped oscillator without inertial term. The resonance frequency is determined by the damping term from the viscous torques and the electrical and elastic torques that drive the director field. With increasing offset voltage, the latter torques increase approximately proportional to U_0^2, and the effective viscosities decrease due to flow coupling, which leads to a noticeable rise in the transition frequency.

Our method provides an easy tool for the determination of the dynamic characteristics of a nematic cell. It is not restricted to planar cells but could as well be applied to any other configuration like TN, STN, homeotropic, or hybrid cells.

The simulated curves of the optical transmission versus voltage curves were fitted to the experimental data with a multidimensional minimization algorithm varying the parameters γ_1, γ_2, η_b, and α_1. As the different viscosity coefficients influence the switching of the cell with different weights, we have performed repeated fits starting from different initial sets of parameters. The results are shown in Figs. 5–10. The figures display the fitted values of the four coefficients at five different temperatures. α_2 and α_3 are calculated from γ_1 and γ_2 with Eq. (3). Crosses denote the

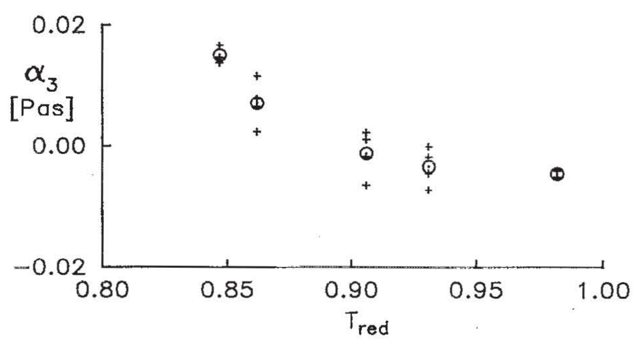

FIG. 9. Leslie viscosity coefficient α_3 calculated using Eq. (3). The crosses are values obtained by fitting the calculated transmission to the measured ones for several offset voltages. The circles give the average values.

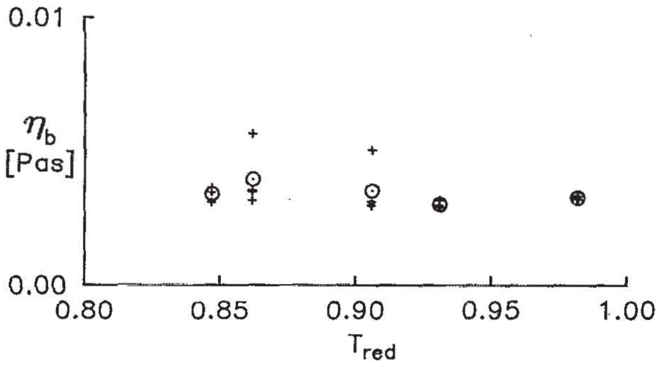

FIG. 10. Shear viscosity η_b. The crosses are values obtained by fitting the calculated transmission to the measured ones for several offset voltages. The circles give the average values.

results of individual fits at different offset voltages of the experimental transmission curve, circles give the average value of all fittings at one temperature. Naturally, the value of γ_1 is determined with high accuracy, whereas the influence of the other viscosities on the switching behavior is weaker and thus the fitted values are less stable. As expected, the determined values $\gamma_2=\alpha_2+\alpha_3$ are nearly equal to $-\gamma_1=\alpha_3-\alpha_2$ within the experimental error. In nematic liquid crystals, consisting of prolate molecules, α_3 is always found to be much smaller than the other viscosities, usually by one order of magnitude (see, e.g., Ref. 3). The coefficients α_1 and η_b are determined with lower accuracy, the error is approximately 20%.

The accuracy of the determined viscosity coefficients (except for γ_1) is certainly not very high, and there are methods that provide a more accurate determination. But if one considers the fact that there are only very few experimental data available in general, that only few experimentalists can access the specialized techniques for a direct measurement of shear viscosities in nematics, and that other techniques like light scattering give a rather indirect method for the determination of these coefficients, our method may be an acceptable alternative. It allows the direct determination of the viscosities, is based on a very simple experimental setup, and needs practically no further assumptions or simplifications. The involved elastic constants are determined with the same equipment at the same sample in an independent experiment. All viscosities are determined in one experiment, and the large amount of experimental data (amplitudes and phases of the optical transmission as a function of frequency f_m and offset voltage U_0) is sufficient for a relatively stable fitting of the four independent parameters.

The sensitivity of the method might be further increased if cells with higher optical phase retardation are used (larger n_e-n_o or larger d). Then, the number of slopes in the transmission curve is increased and one may have access to higher U_0/U_c offset voltages where the effect of the flow coupling (α_2,η_b) is larger.

ACKNOWLEDGMENT

This work was supported by the Deutsche Forschungsgemeinschaft under grants Tr 154/7-1 and Schm 902/2-1. The authors would like to express their thanks to E. Merck, Darmstadt, Germany, for providing the nematic mixture ZLI 2293.

[1] P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1974).
[2] B. Kiebs and K. Eidner, Wiss. Zeitschr. KMU Leipzig, Naturwiss. Reihe **30**, 197 (1981).
[3] H. Kneppe, F. Schneider, and N. K. Sharma, J. Chem. Phys. **77**, 3203 (1982).
[4] H. H. Graf, H. Kneppe, and F. Schneider, Mol. Phys. **77**, 521 (1992).
[5] A. F. Martins, P. Esnault, and F. Volino, Phys. Rev. Lett. **57**, 1745 (1986).
[6] M. Miesowicz, Bull. Int. Acad. Polonia A 228 (1936); Fizyka Dielekt. i Radiospect. XI/2, 135 (1979).
[7] A. Scharkowski, H. Schmiedel, R. Stannarius, and E. Weisshuhn, Z. Naturforsch. **45a**, 37 (1990).
[8] P. Pieranski, F. Brochard, and E. Guyon, J. Phys. (Paris) Colloq. **34**, 35 (1973).
[9] F. M. Leslie, Quart. J. Mech. Appl. Math. **19**, 357 (1966).
[10] J. L. Ericksen, Arch. Rat. Mech. Anal. **4**, 231 (1960).
[11] C. Z. van Doorn, J. Appl. Phys. **46**, 3738 (1975).