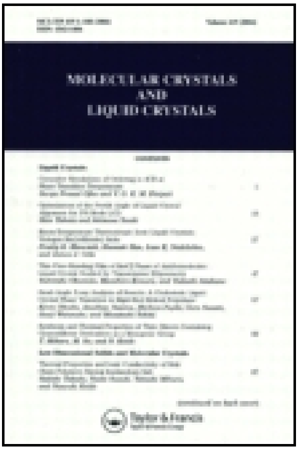

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006

Mol. Cryst. Liq. Cryst., 1999, Vol. 329, pp. 533-538
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Homeotropic nematic layers of MBBA oriented by self-assembled monolayers of CTAB were studied by phase-sensitive flexoelectric spectroscopy method. Higher frequency part of the viscoelastic spectra provided information about surface dissipation of orientational energy. Temperature dependence of surface viscosity was revealed for the first time. Influence of area density of CTAB monolayer was also investigated.

Keywords: flexoelectric spectroscopy; weak anchoring; surface viscosity

INTRODUCTION

In a previous paper the first experimental observation of nematic surface viscosity by the method of flexoelectric spectroscopy was reported[1]. Knowledge of this parameter can reveal important dynamic aspects of the orientational interaction nematic-substrate and of the surface dissipation of energy. In this work temperature dependence of surface viscosity of MBBA/CTAB interface is systematically investigated.

THEORY

Flexoelectric spectroscopy was carried out by the method and device for generation and amplification of flexoelectrooptic oscillations of light passing through a homeotropic nematic layer[1]. Our method essentially consists in the simultaneous application of an a.c. field $E_1 \cos\omega t$ to a homeotropic sample of thickness d and a d.c. bias E_0, creating a static bend deformation over which the surface-torque-driven flexooscillations are superimposed. The d.c. bias leads to a displacement of the electrooptic system (consisting of two crossed polarizers with the homeotropic layer between them, and with electric field applied at 45° to the polarization plane, see figure 1) from the minimum transmittance and to the appearance of 1st harmonic in the modulated light intensity. Theoretically, the problem for the description of these oscillations is described elsewhere[2]. Following that general theoretical scheme we extended our original solution and we report here an expression for the frequency spectrum (i.e. frequency dependence of the first harmonic amplitude) that is valid in the whole range of frequencies employed (0.1 - 3 kHz) and includes surface anchoring (b), bulk viscosity (γ_1^*) and surface viscosity (κ) contributions:

$$I_\omega = \frac{A}{\omega}\frac{1 - \frac{B}{d}\frac{1}{\sqrt{\omega}}}{\sqrt{\left(1 + \frac{B}{b}\frac{1}{\sqrt{\omega}}\right)^2 + \left(1 - D\sqrt{\omega}\right)^2}} \qquad (1)$$

where

$$A \propto \frac{2 e_{3x}^{*4} E_1 E_0^3 d^4}{3 K_{33}^3 \gamma_1^* (1 + d/2b)^3}; \quad B = \sqrt{\frac{2K_{33}}{\gamma_1^*}}; \quad D = \kappa\sqrt{\frac{2}{K_{33}\gamma_1^*}}; \quad b = \frac{K_{33}}{C}$$

Here $e_{3x}^* = e_{3x} + m_p$ is the bend flexocoefficient *plus* surface polarization, K_{33} is the bend elastic constant, γ_1^* is the rotational viscosity of the nematic, corrected for the back-flow, κ is the surface viscosity and C is the anchoring energy. By fitting the above expression to the experimentally obtained flexoelectric spectra we can find the parameter D and surface viscosity κ, providing K_{33} and γ_1^* are known. Further, this suggests the opportunity to reveal the temperature dependence of surface viscosity κ.

MATERIALS AND METHODS

Nematic layers of MBBA (T_C = 43°C) obtained from Reachim were studied throughout. The nematic material was sandwiched between two glass plates with homeotropic treatment of the glass surfaces. CTAB monolayers (cetyltrimethylammonium bromide) were used as orientants. The CTAB monolayer films were self-assembled by dipping the precleaned substrates into water solutions of the surfactant CTAB (Merck 99% p.a.) at $1.6 \cdot 10^{-5}$ M concentration in bidistilled water for 10 min. The plates were then withdrawn using a self-made device with two different speeds of 0.6 cm/min and 2 cm/min to obtain densely packed and loosely packed orienting films for homeotropic MBBA anchoring[3]. Care was taken that the plates emerge completely dry from the solution.

Liquid crystal cells were assembled with 100 μm thick Cu-foil spacers serving as electrodes. The samples were sealed by Araldite (epoxy-glue). The inter-electrode distance was 2 mm. Cells were filled at room temperature by capillarity and placed in a Mettler FP82 heating stage for varying the temperature. The samples' homeotropic orientation was proven by conoscopic images. Homeotropic nematic cells were arranged between crossed polarizers. A horizontal electric field directed at 45° versus crossed polarizers was applied to the nematic layer by means of the copper spacers.

The frequency dependence of transmitted light modulation was obtained by means of a flexoelectric spectrometer comprising an universal polarizing microscope (NU-2, Zeiss), a 1mW red light laser diode (laser pointer) as a light source, a computer-driven Lock-in Amplifier Model SR830 DSP and a phototransistor. A logarithmic frequency sweep for a user-defined range and rate was selected from the PC, amplified by an external self-made amplifier and applied to the sample. The d.c. bias was provided by the same amplifier. With this system measurements of director dynamics in the low frequency range (up to a few kHz) are possible. 1st harmonic vs. frequency spectra revealed important information about the surface viscoelastic properties.

RESULTS AND DISCUSSION

In Fig. 1, the 1st harmonic flexoelectric spectra of MBBA anchored on a loose CTAB monolayer (corresponding to 2 cm/min pulling velocity) at different temperatures in the nematic range are displayed. The shape of the spectra closely follows theoretical predictions: in the lower end $I_\omega \propto \omega^{-1}$ and in the higher end $I_\omega \propto \omega^{-1.5}$. This is well seen from the fit made for the 31.0°C curve.

In the studied frequency range above 1 Hz the two terms in Eq. (1) containing the parameter B are negligible. Therefore, a two-parametric fit with A and D as parameters was performed.

It is seen that the cross-over frequency decreases with increasing the temperature. By means of the described fitting procedure, the values of parameter D were extracted and surface viscosity was calculated. To this aim data for γ_1^* and K_{33} for the corresponding relative temperatures of MBBA were interpolated from Figs. 9 and 10 in[4]. The calculated values of κ are shown in Fig. 2.

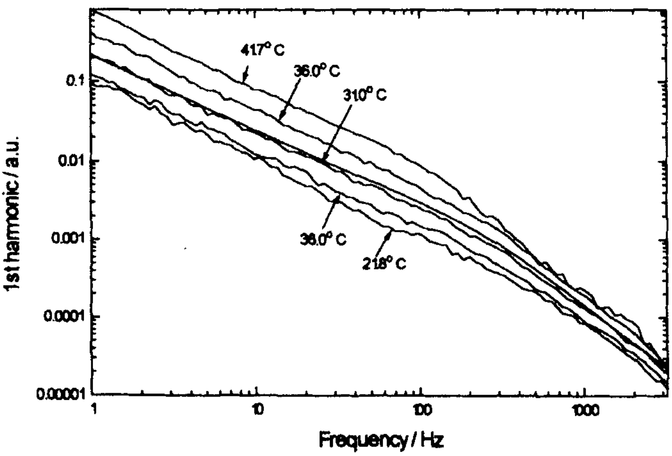

FIGURE 1 Frequency dependence of the 1st harmonic of flexo-electrically modulated transmitted light through a homeotropic nematic layer of MBBA at different temperatures. Homeotropic orientation by a loose CTAB monolayer (bulk concentration $1.6 \cdot 10^{-5}$ M, 2 cm/min pulling velocity of the glass substrate). The temperature shift of the cross-over frequency is evident. Layer thickness is 100 μm, electrode distance is 2mm, a.c. voltage is 30 V_{pp}, d.c. bias is 30 V. For the sake of clarity only one fit of the spectrum at 31.0°C is shown on the graph.

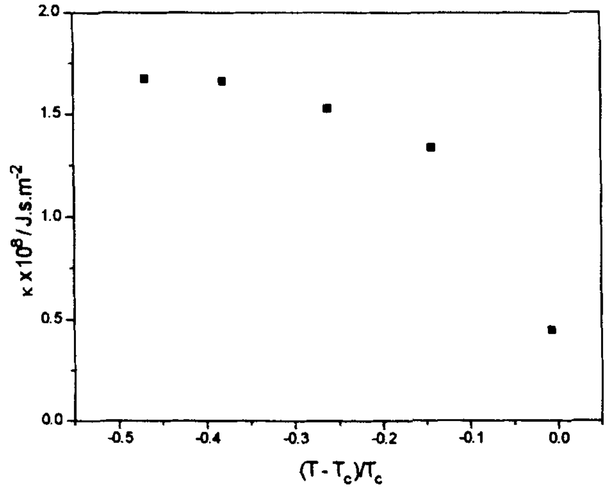

FIGURE 2 Temperature dependence of surface viscosity of MBBA homeotropic nematic layer in contact with loose self-organized films of CTAB (bulk concentration $1.6 \cdot 10^{-5}$ M, 2 cm/min pulling velocity of the glass substrate, 100 μm thickness of LC layer).

At still higher velocity of pulling the substrates (more than 2 cm/min) no homeotropic ordering is achieved. At lower pulling velocity (0.6 cm/min) good homeotropic orientation is obtained. However, in comparison with the loosely covered substrates at higher pulling speeds, a middle frequency plateau appears on the spectral curve, not explainable by the present theory. This interesting phenomenon is observed also with orienting layers of lecithin, self-assembled by dipping in chloroform solution. The middle frequency plateau may be due to the formation of a gradient of the excess surfactant close to the substrate. It will be the object of future investigations.

CONCLUSION

Theoretical and experimental results of the dynamics of flexoelectric oscillations presented here demonstrate the good agreement of the theoretical model for surface dissipation of energy in terms of surface viscosity in the case of a minor amount of orienting substance, that is a negligible surfactant gradient near the substrate. The room temperature value of $\kappa = 1.67 \cdot 10^{-8}$ J s m^{-2} for MBBA/CTAB interface is in a good correspondence with the value $\kappa = 2.6 \cdot 10^{-8}$ J s m^{-2} for MBBA/DMOAP(polymerized) interface, reported by us previously[1].

Acknowledgments

This work is supported by INCO-COPERNICUS (ERBIC15-CT96-0744) joint project and by the National Fund "Scientific Studies"of Bulgaria (Project F519).

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