

Surface Dissipation in Homeotropic Nematic Layers Characterized by Orientant Desorption*

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Abstract. Viscoelastic spectra of homeotropic nematic layers of MBBA oriented by self-assembled films with different degree of desorption: high (dilauryl phosphatidyl choline, DLPC) and low (chromolan) have been studied by a phase-sensitive flexoelectric spectroscopy method. Orientants desorb from the surface and dissolve in the nematic, producing a surface gradient of concentration of the orientant. Extended theoretical treatment was implemented resulting in spectral shapes, which have been successfully compared to the experiment, yielding information about the surfactant gradient. These results permit us to reveal the existence and the structure of a desorbed layer of orientant in homeotropic oriented nematics.

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1 Introduction

In our recent study [1] on surface dissipation of orientational energy in homeotropic nematic layers a considerable deviation of experimental data from theory [2-4] for non-desorbable orientants was found. It was ascribed to the presence of the surfactant gradient concentration close to the orienting surfaces. Now further extension of the theory is implemented taking into account space variation of the characterizing the nematic state parameters.

*This work is dedicated to Professor Alexander Derzhanski, DSci., Corresponding Member of the Bulgarian Academy of Sciences, on the occasion of his 70th anniversary.

In the present paper the effect of surfactant desorption have been analyzed by comparing of the theoretically predicted spectral shapes to the experimentally obtained flexoelectric spectra. Some parameters of desorbed surface layer as the thickness and the bend flexocoefficient have been discussed. We have measured the first harmonic in the flexoelectrically modulated light passing through a homeotropic nematic layer subjected to DC+AC electric field parallel to the layer plane, following a slow frequency sweep.

2 Theory

The flexoelectric spectroscopy method, essentially consists in the simultaneous application of an AC field $E_1 \cos \omega t$ to a homeotropic nematic layer of thickness d and DC bias E_0 , creating a static bend deformation over which the surface-torque-driven flexooscillations are superimposed. The homeotropic sample is placed between two crossed polarisers and electric field E_0 is applied at 45° to the polarization plane. DC bias leads to a displacement 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 [4]. Generalizing the existing theory with non-desorption [2-4] we have obtained (detailed description is published elsewhere [5]) the following expressions for the spectral curve shape of the first harmonic amplitude of the viscoelastic flexoelectrically excited oscillations of transmitted light intensity in presence of a surface desorbed layer.

$$R(\omega) = \frac{1}{\omega} \sqrt{\left(P_4 \exp(-P_5 \sqrt{\omega}) \right) + \left(P_1^2 + 2P_2 \frac{P_2 + P_1(2 - P_3 \sqrt{\omega})}{1 + (1 - P_3 \sqrt{\omega})^2} \right)} \quad (1)$$

where

$$P_1 = \frac{1}{3} \left(I_0 \frac{\pi^2}{\lambda^2} \right) \Delta n_B^2 \frac{e_B^3}{k_B^3} \frac{e_B - e_S}{k_B} E_0^3 E_1 d^3 \left[\frac{1 - \left(\frac{e_S}{e_B} - 1 \right) \frac{d}{2b}}{1 + d/2b} \right]^3 \frac{k_b}{\gamma_B} d \quad (2)$$

$$P_2 = \frac{1}{3} \left(I_0 \frac{\pi^2}{\lambda^2} \right) \Delta n_S \Delta n_B \left[\frac{e_S}{k_S} \frac{e_B}{k_B} \right]^2 E_0^3 E_1 d^3 \frac{\left[1 - \left(\frac{e_S}{e_B} - 1 \right) \frac{d}{2b} \right]^2}{[1 + d/2b]^3} \frac{k_S}{\gamma_S} d \quad (3)$$

$$P_3 = \chi \sqrt{\frac{2}{k_S \gamma_S}} \quad (4)$$

$$P_5 = \delta \sqrt{\frac{\gamma_S}{2k_S}} \quad (5)$$

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Here I_0 is the incoming light intensity, k is the bend elastic constant, e is the bend flexoelectric coefficient, γ is the bulk viscosity, χ is the surface viscosity, λ is the light wavelength, δ is the thickness of the surface layer, ω is the angular frequency, P_4 is the fitting parameter [5], $b = k_s/W$ is the extrapolation length, W is the anchoring strength at the surfaces of the sample, d is the sample thickness and Δn is the birefringence. Subscripts S and B indicate the physical parameters characterizing the liquid crystal in the surface layer and in the bulk, respectively. Experimentally, it is suitable to perform the fit to the spectral shape multiplied to the angular frequency at each point. In this way deviations of the fit from the experiment are better expressed. By fitting the flexoelectric spectra we can extract the parameters P_3 and P_5 and find the surface viscosity χ and thickness δ of the desorbed layer.

3 Materials and Methods

The MBBA (clearing point $T_c = 43^\circ\text{C}$, Reachim) layers are homeotropically oriented by synthetic lecithin (DLPC) or Chromolan (from NIOPIK, see Figure 1) by dipping method employed to the precleaned glass substrates. Glass plates were dipped in chloroform solution at 0.15 mM concentration for 20 min and then air-dried at 50°C to obtain self-assembled DLPC multilayers. For comparison self-assembled chromolan layers were prepared by dipping the glass plates in chromolan/iso-propyl alcohol solution at 0.4 wt% for 20 min then air-dried at 120°C for 120 min.

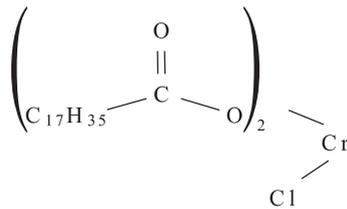


Figure 1. Chemical formula of Chromolan

Liquid crystal cells were assembled with $100\mu\text{m}$ thick Cu-foil spacers serving as electrodes. The samples were sealed by Araldite (epoxy-glyce). The inter-electrode distance was 2 mm. Cells were placed in a Mettler FP82 heating stage for varying the temperature. The frequency dependence of transmitted light modulation depth was obtained by means of a “flexoelectric spectrometer” [2-3].

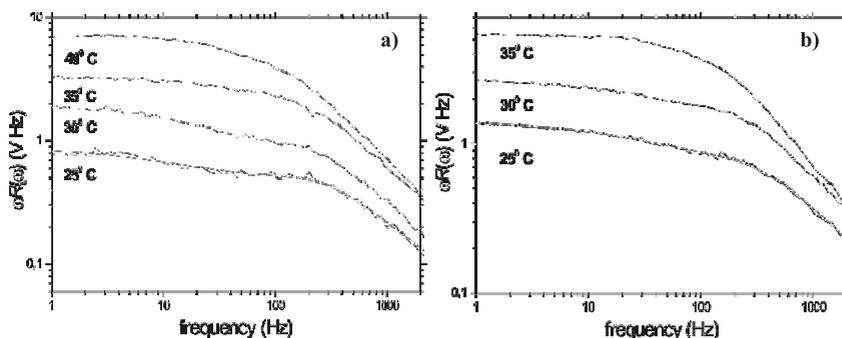


Figure 2. Frequency dependence (multiplied by ω) of the first harmonic of flexoelectrically modulated transmitted light through a homeotropic nematic layer of MBBA at different temperatures (Log-Log Plot). Layer thickness is $100 \mu\text{m}$, electrode distance is 2 mm : **a)** homeotropic orientation by self-assembled DLPC layers (bulk concentration 0.3 mM), d.c. voltage $40 V_{pp}$; **b)** homeotropic orientation by self-assembled Chromolan layers (bulk concentration 1 mM), d.c. voltage $30 V_{pp}$. The fits are reported for the spectra at 25°C (smooth lines). The fit coefficients are shown on Tables 1 and 2

4 Results and Discussion

With both surfactants weak homeotropic anchoring was achieved. Flexoelectric spectroscopy yields spectral shapes (Figure 2) that are fitted by 5 parameters, listed in Table. For better revealing of spectral shape features, renormalization of the spectrum for the overall ω^{-1} slope was made. These plots clearly show that the extension of the theory provides a reasonable fit over the whole

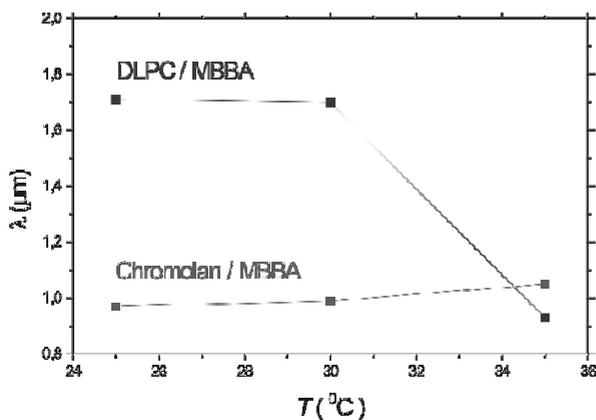


Figure 3. Temperature dependence of the thickness of a desorbed layer formed by partially dissolving of DLPC and Chromolan in MBBA

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frequency range. In comparison with the DLPC orientant a middle frequency 'plateau' situated in the range from 20 Hz to 200 Hz (it is better expressed in the lower temperature spectra, Figure 2a) is not observed with chromolan orientant (Figure 2b) even in the range of low temperatures. By means of the parameter P_5 (Eq. 5) we can estimate the thickness of the desorbed layer. In the Figure 3 the thickness of desorbed layer is calculated as a function of temperature. Upon temperature increasing, it is seen that the thickness of desorbed DLPC layer decreases while the chromolan one stays more or less constant. Detailed discussion of present experimental findings will be given in a future paper.

According to our data (Table 1 and 2) $P_1 > 0$. In this case equation (2) gives that the bulk flexocoefficient is higher than the flexocoefficient of the surface layer: $e_B > e_S$. This fact is very important and can significantly change the actual values of the bend flexoelectric coefficients evaluated by the various methods not taking into account surfactant desorption.

Table 1.

| T (°C) | χ^2 | P_1 | P_2 | P_3 | P_4 | P_5 |
|----------|----------|-------|-------|-------|--------|-------|
| 25 | 0.001 | 0.063 | 0.318 | 0.034 | 0.746 | 0.124 |
| 30 | 0.002 | 0.117 | 0.529 | 0.036 | 4.423 | 0.112 |
| 35 | 0.003 | 0.236 | 1.007 | 0.047 | 10.546 | 0.050 |
| 40 | 0.014 | 0.247 | 2.705 | 0.104 | 48.030 | 0.060 |

Table 2.

| T (°C) | χ^2 | P_1 | P_2 | P_3 | P_4 | P_5 |
|----------|----------|-------|-------|-------|--------|-------|
| 25 | 0.001 | 0.023 | 0.466 | 0.032 | 1.974 | 0.071 |
| 30 | 0.001 | 0.240 | 0.851 | 0.035 | 6.880 | 0.066 |
| 35 | 0.007 | 0.324 | 2.381 | 0.068 | 24.277 | 0.058 |
| 45 | — | — | — | — | — | — |
| 35 | 0.005 | 0.307 | 1.366 | 0.085 | 27.395 | 0.048 |
| 30 | 0.007 | 0.268 | 1.168 | 0.207 | 14.679 | 0.050 |
| 25 | 0.002 | 0.187 | 0.752 | 0.039 | 8.741 | 0.127 |
| 20 | 0.002 | 0.135 | 0.558 | 0.038 | 3.851 | 0.165 |

5 Conclusion

The extension of the theory reported here permits us to reveal the existence and the structure of a desorbed layer of orientant in homeotropic nematics in some details. The thickness of this layer depends on the type of orientant and may decrease with temperature (DLPC) or remains essentially constant (chromolan). The positive sign of parameter P_1 means that the flexocoefficient of the surface layer is less than that the undisturbed bulk value in the case of both orientants.

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