

SURFACTANT DESORPTION IN HOMEOTROPIC NEMATIC LAYERS STUDIED BY FLEXOELECTRIC SPECTROSCOPY

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Homeotropic nematic layers of MBBA and BMAOB liquid crystals, oriented by self-assembled films (on glass plates) of dilauroyl phosphatidyl choline (DLPC) and chromolan have been studied by a phase-sensitive flexoelectric spectroscopy method [1-3]. The viscoelastic spectra of these layers, reflecting the surface dissipation of the orientational energy, have been analyzed taking into account a strong (DLPC) or weak (chromolan) surfactant desorption. Surfactant molecules desorb from the surface and dissolve in the nematic, producing a surface gradient of the concentration of the surfactant. A theoretical treatment of the first harmonic [4] has been implemented. The temperature dependence of the thickness of the desorbed subsurface layer of the surfactant was revealed. The surface viscosity was also obtained from the theoretical fits to the spectra. These results are able to give new insights on the physics of the nematic liquid crystal - solid surface interaction, where flexoelectricity and surfactant desorption play a fundamental role.

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1. Introduction

This study aims to implement the theory of surfactant desorption into liquid crystals [4] and to compare the predicted spectral shapes to the experimental ones for the cases of a strong (DLPC) or weak (chromolan) surfactant desorption. The method of flexoelectric spectroscopy is applied [1,2]. The first harmonic in the flexoelectrically modulated light intensity, passing through the homeotropic layer subjected to a DC+AC electric field parallel to the cell plates, is measured, following a slow frequency sweep provided by a computer-interfaced lock-in amplifier (SR830).

2. Experimental details

Generalizing the theory of the no desorption case, we have obtained an expression for the shape of viscoelastic, flexoelectrically excited oscillations of transmitted the light intensity [3,4]:

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

where:

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

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

$$P_3 = \chi \sqrt{\frac{2}{k_S \gamma_S}} \quad ; \quad P_5 = \delta \sqrt{\frac{\gamma_S}{2k_S}} \quad (4)$$

Here, I_0 is the incoming light intensity, k is the bend elastic constant, e 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 [4], $b = k_s/W$ 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. The 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 by the angular frequency at each point. In this way deviations of the fit from the experiment are better expressed.

MBBA and BMAOB layers between glass plates are homeotropically oriented by synthetic Dilauroyl Phosphatidyl Choline (DLPC) and Chromolan deposited by a substrate dipping method.

3. Results and discussion

Flexoelectric spectroscopy yields spectral shapes (Figs. 1a and 1b) that are fitted according eq. (1) by 5 parameters, listed in Tables 1 and 2 for MBBA. From the parameter P_5 , the thickness δ of the desorbed layers orienting MBBA is calculated according to eq. (4), as a function of temperature (Fig. 3). Homeotropic nematic layers of BMAOB, oriented by Chromolan are also studied (Fig. 2; Table 3).

Table 1. Fit parameters for the flexoelectric spectra of the MBBA/DLPC layer.

T(°C)	Chi ²	P ₁	P ₂	P ₃	P ₄	P ₅
30	1.10 ⁻³	0.010	0.381	0.092	1.106	0.038
35	1.10 ⁻³	0.098	0.600	0.076	2.862	0.046
39.5	1.10 ⁻³	0.092	0.702	0.061	2.758	0.059
35	3.10 ⁻³	0.004	0.686	0.067	1.095	0.054
30	3.10 ⁻⁴	0.039	0.252	0.147	2.291	0.043
25	1.10 ⁻³	0.020	0.471	0.343	1.251	0.041

Table 2. Fit parameters for the flexoelectric spectra of the MBBA/Chromolan layer.

T(°C)	Chi ²	P ₁	P ₂	P ₃	P ₄	P ₅
25	1.10 ⁻³	0.063	0.318	0.034	0.746	0.124
30	2.10 ⁻³	0.117	0.529	0.036	4.423	0.112
35	3.10 ⁻³	0.236	1.007	0.047	10.55	0.050

Table 3. Fit parameters for the flexoelectric spectra of the BMAOB/Chromolan layer.

T(°C)	Chi ²	P ₁	P ₂	P ₃	P ₄	P ₅
45	2.10 ⁻²	0.237	3.404	0.148	44.21	0.041
55	3.10 ⁻¹	0.426	3.878	0.174	88.03	0.047
65	8.10 ⁻²	0.407	1.317	0.043	189.2	0.319
73	1.10 ⁻²	0.349	0.598	0.034	51.32	0.487

It is easily seen (Fig. 3) that in the case of DLPC, the thickness of the orienting layer increases at higher temperatures. However, in the case of Chromolan it changes only slightly indicating weak desorption of the surfactant. According to our data (Tables 1 - 3) P_1 is greater than 0. In this case, equation (2) indicates that the bulk flexocoefficient is higher than the flexocoefficient of the surface layer: $e_B > e_S$. This is very important for the actual values of the bend flexoelectric coefficients, in contrast to the values evaluated by other methods not taking into account surfactant desorption. From the parameter P3, the surface viscosity at room temperature of the above liquid crystals for the applied surfactants is extracted, as in Table 4. It is evident that the kind of surfactant slightly influences the surface viscosity value in the case of MBBA.

Table 4. Surface viscosity ($\kappa 10^8 / \text{J.s.m}^{-2}$) at room temperature of two liquid crystals, MBBA and BMAOB, homeotropically oriented by DLPC and Chromolan.

Liquid crystal	Chromolan	DLPC
MBBA	2.1	2.0
BMAOB	2.3	-

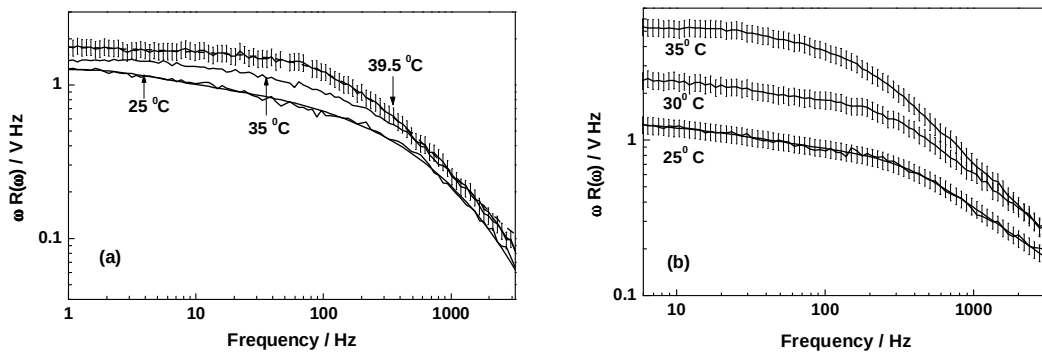


Fig. 1. Frequency dependence (multiplied by ω) of the first harmonic of flexo-electrically modulated transmitted light through a homeotropic nematic layer of MBBA at different temperatures. The layer thickness is 100 μm , and the electrode distance is 2 mm: a) homeotropic orientation by self-assembled DLPC layers (bulk concentration 0.15 mM), voltage 50 V_{pp} . b) homeotropic orientation by self-assembled Chromolan layers (bulk concentration 1mM), voltage 30 V_{pp} .

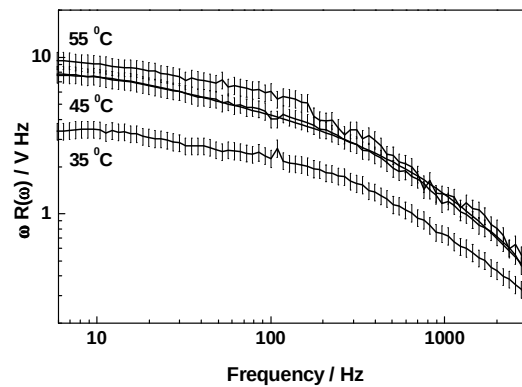


Fig. 2. Frequency dependence (multiplied by ω) of the first harmonic of flexo-electrically modulated transmitted light through a homeotropic nematic layer of BMAOB at different temperatures. The layer thickness is 100 μm , and the electrode distance is 2 mm; homeotropic orientation by self-assembled Chromolan layers (bulk concentration 1mM), voltage 30 V_{pp} .

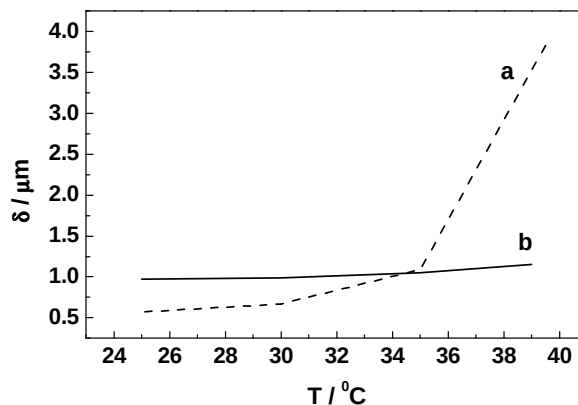


Fig. 3. Thickness of desorbed layers as a function of the temperature: a) MBBA homeotropically oriented by DLPC, b) MBBA homeotropically oriented by Chromolan.

4. Conclusions

The extended theory, employed here, reveals the existence and structure of a desorbed layer of surfactant in homeotropic nematics, in some detail. The thickness of this layer depends on the type of surfactant and may increase with temperature (DLPC) or remain essentially constant (Chromolan). The positive sign of the parameter $P1$ means that the flexocoefficient of the surface layer is less than the undisturbed bulk value in the case of both surfactants.

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References

- [1] A. G. Petrov, A. Th. Ionescu, C. Versace, N. Scaramuzza, *Liquid Crystals* **19**, 169 (1995).
- [2] Y. Marinov, N. Shonova, C. Versace, A. G. Petrov, *Mol. Cryst. Liq. Cryst.* **329**, 533 (1999).
- [3] Y. Marinov, N. Shonova, S. Naydenova, A. G. Petrov, *Mol. Cryst. Liq. Cryst.* **351**, 411 (2000).
- [4] S. Ponti, Y. Marinov, G. Barbero, A. Strigazzi, A. G. Petrov, *Mol. Cryst. Liq. Cryst.*, in press.