Effect of a surfactant on the electro-optic response in ferroelectric liquid crystals

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The interaction of mobile surfactant ions in the alignment layer and the surface charges produced by the spontaneous polarization of a ferroelectric liquid crystal (FLC) leads to the appearance of a monostable response of the FLC. The source of the monostability is the internal field produced in the FLC by the surfactant ions in the alignment layer.

A ferroelectric liquid crystal[1] (FLC) exhibits two types of characteristic electro-optic responses in a geometry with an unwound helix.[2] The first type is characterized by different, temporally stable orientations which are established for the FLC molecules (different directions of the director FLC) after the opposite polarities of the external electric field **E** are switched off. This response is due to the dispersion interaction of the FLC molecules and the alignment layer and it is bistable.[2] The presence of spontaneous polarization $\mathbf{P}_s$ in the FCL[1] leads to the formation of a surface charge on the interface between the FLC and the alignment layer and therefore to the formation of an internal field $\mathbf{E}_p$ in the FLC and in the alignment layers.[3] It is well known[4] that ions of different origin are always present in the volume of a liquid crystal. Under the action of the internal field $\mathbf{E}_p$ these volume ions move toward the surfaces bounding the FLC.[5] If $\mathbf{P}_s$ is now reversed by an external-field pulse, then as result of the interaction with the volume ions which have accumulated on the surfaces, the new direction of $\mathbf{P}_s$ and the corresponding direction of the director of the FLC become unstable and switch into the initial state. Such a response is monostable[5] and the switching time changes when the sign-alternating pulses are applied as the ions leave the surface and migrate into the volume of the FLC.

Monostability can be avoided either by decreasing the magnitude of the spontaneous polarization $\mathbf{P}_s$ to 20 nC/cm^2 or less,[3] which makes $\mathbf{E}_p$ less than a critical value, or by introducing into the orienting agent conducting additives, for example, complexes with charge transfer.[6] Additives are introduced in order to achieve virtually instantaneous compensation of an arbitrarily oriented internal field $\mathbf{E}_p$.

In the present paper we show that when an ionic surfactant is added to the orienting agent, the observed response of the FLC cell is opposite to the expected response. For example, for $\mathbf{P}_s = 5$ nC/cm^2 a monostable response with a switching time of up to tens of milliseconds is observed.

The materials ZhKSM-1008 and ZhKSM-1011, for which $\mathbf{P}_s = 5$ nC/cm^2 and 10 nC/cm^2, respectively, and a SmF ← SmA transition temperature $T_{CA} = 51\,^\circ\mathrm{C}$ were used as the FLC. These materials were developed at the Scientific-Research Institute of Or-

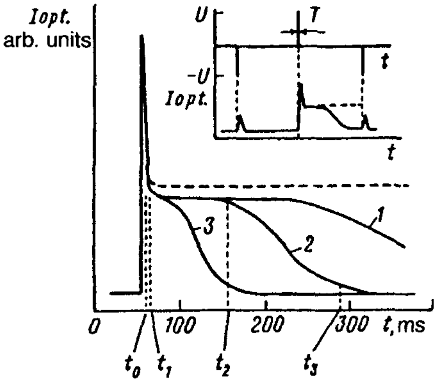

FIG. 1. Oscillograms of the optical response $I_{\rm opt}$ to applied voltage pulses (shown in the inset). The times t_2 and t_3 refer only to curve *2*. The conditions under which the response was observed are: $T=23°{\rm C}$, $U=20$ V, and the pulse duration is 100 μs. Curve *1* — $P_s=5$ nC/cm^2, 15 wt.% surfactant in solution with the polymer; *2* — $P_s=5$ nC/cm^2, 22% surfactant; *3* — $P_s=10$ nC/cm^2, 15% surfactant. The dashed line represents the bistable response; $P_s=10$ nC/cm^2 and no surfactant in the alignment layer.

ganic Intermediates and Dyes. The surfactant is of the ionic type[7,8] and its chemical formula is $[C_{17}H_{35}COOCr_2OH]^{+4}\cdot 4Cl^-$.

The surfactant was mixed in different proportions with a polymer in dimethylformamide. Next, to produce the alignment layers, the solution obtained was deposited on a substrate in a centrifuge with a rotational speed of 3700 rpm. After drying at $T=200°{\rm C}$ for 1 h the layers were rubbed in order to align the FCL molecules. The experimental cells were filled with the FLC materials, which were in an isotropic phase. The electro-optic properties of the cells were investigated in crossed polaroids at room temperature. A chevron structure of the smectic layers forms in the experimental cells and the orientational states of the director of the FLC (dependence of the direction of the director in the SmF phase on the coordinate along the normal to the substrate) are uniform.[9] There are no twist states[9] in the texture.

Oscillograms of the electro-optic responses of the experimental FLC cells are shown in Fig. 1. The response peaks obtained when the voltage pulses are applied (see Fig. 1) are associated with the perturbation of the stable orientational state of the director, which was obtained as the cell was cooled after being filled, by the electric field of these pulses. After the positive pulse is switched off at the time t_0 under the action of other forces, the perturbed state at first relaxes to an unstable state, which exists for time t_2-t_1, and then to the initial stable state. The switching between the unstable and stable states occurs over a time t_3-t_2 via a domain wall.[10]

An asymmetry of the extinction angles of the stable and unstable states relative to the direction of rubbing is observed in the experimental cells and the switching time t_3-t_2 depends on P_s (oscillograms *1* and *3* in Fig. 1) and on the amount of surfactant in the solution (oscillograms *1* and *2* in Fig. 1). This suggests to us that an internal electric field $\mathbf{E}_{\rm int}$, which induces the switching, is present in the volume of the FLC. Here the source of this field is the surfactant ions. We also note the following experimental facts:

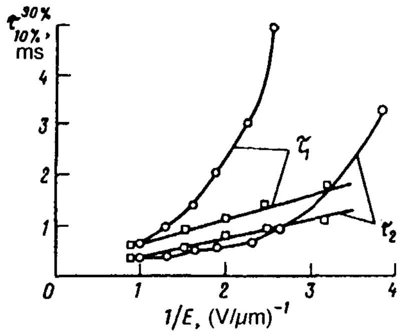

FIG. 2. Optical response times $\tau_{10\%}^{90\%}$ as a function of the strength of the external electric field E. The time τ_1 corresponds to oppositely oriented fields $\mathbf{E}$ and $\mathbf{E}_{\text{int}}$ (see text), τ_2 — same orientations. ○ — $P_s = 10$ nC/cm^2, 15% surfactant; □ — $P_s = 10$ nC/cm^2 and no surfactant in the alignment layer.

1) No increase is observed in the conductivity of the FLC when a surfactant is added to the orienting agent; 2) the time interval $t_3 - t_2$ at room temperatures does not change with time and therefore $\mathbf{E}_{\text{int}}$ is also stable in time; and 3) the field $\mathbf{E}_{\text{int}}$ is oriented in the same direction as the direction of $\mathbf{P}_s$ which was established by the phase transition SmA →SmF.

We propose the following model to explain the observations described above. Since the ionic surfactant in solution dissociates into ions, we assume that ions with different signs are present in the alignment layer, which remains neutral as a whole. At temperatures $T < T_{CA}$ spontaneous-polarization charges appear on the surfaces of the alignment layers. These charges produce an electric field in the layers and in the volume of the FLC. Under the action of this field surfactant ions move in the volume of the alignment layers, and the above-described volume ions move in the volume of the FCL. Since $\mathbf{E}_p$ is weak,[3] we ignore the motion of the corresponding volume ions in the volume of the FLC. At room temperature, where the temperature dependence of P_s saturates,[10] because of the assumed activational character of the motion of the surfactant ions, the volume distribution obtained for these ions in the alignment layer "freezes," which causes the formation of an internal field $\mathbf{E}_{\text{int}}$ that remains quite stable over time.

If a field $\mathbf{E}_{\text{int}}$, which is stable in time, is present and if sign-alternating square pulses are applied to the experimental cells, the electro-optic response times of the cells for opposite polarities of the external field $\mathbf{E}$ should be different. The corresponding curves are shown in Fig. 2. Using the formulas[10]

$$\tau_1 = k/(E - E_{\text{int}}), \quad \tau_2 = k/(E + E_{\text{int}}), \tag{1}$$

where k is a coefficient, and the data in Fig. 2, we obtain $E_{\text{int}} \cong 0.24 \pm 0.04$ V/μm. The small difference between τ_1 and τ_2 in the absence of a surfactant in the alignment layer is attributable to the migration of the ions out of the volume of the FLC. However, the response of the cell in this case is bistable (the dashed line in Fig. 1).

We assume, in accordance with the model described above, that the field $\mathbf{E}_{\text{int}}$ of the surfactant ions completely cancels the field $\mathbf{E}_p$ of spontaneous-polarization charges. We find the latter field in the volume of the FLC from the formula[3]

$$E_p = 2P_s d_{or}/(\epsilon_0(d\epsilon_{or} + 2d_{or}\epsilon)), \tag{2}$$

where d_{or} and d are, respectively, the thicknesses of the alignment layer and the FLC; ϵ_{or} and ϵ are the relative permittivities of the orienting agent and the FLC, respectively; ϵ_0 is the permittivity. Substituting into Eq. (2) the actually used parameters $d_{or} = 500$ Å, $d = 1.5$ μm, $\epsilon_{or} = 2.5$, $\epsilon = 5$, and $P_s = 10$ nC/cm^2, we find $E_p = 0.24$ V/μm. The computed value of E_p agrees well with the experimentally determined value of E_{int}; this confirms the correctness of the proposed model.

In conclusion, we note that the method, discovered and described in the present work, for producing in the volume of a FLC a temporally stable, internal field opens up new possibilities for applications of this class of materials.

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