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FLEXOELECTRICITY AND SURFACE POLARIZATION

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Abstract The comparison between experimental condition in two experiments measuring MBBA bend flexocoefficient and an analogy with lyotropic liquid crystals lead to the concept that the reason for the big difference obtained is the opposite direction of the surface polarization due to the hydrophobic or hydrophilic surfaces used and weak amphiphilic character of MBBA molecule.

INTRODUCTION

At present two values can be found in the literature concerning bend flexocoefficient of MBBA. First one was calculated by Helfrich (1) using the experimental data of Haas et al.(2). According to the formula derived by him, Helfrich has found

$$e_{3x}/K_{33} = 340 \text{ dyne}^{-1/2} \quad . \qquad /1/$$

Then, taking for K_{33} the value 8.10^{-7} dyne (3) but not the PAA value 2.10^{-6}dyne as in (1) one can find

$$e^1_{3x} = 2{,}7.10^{-4} \text{ dyne}^{1/2} \quad . \qquad /2/$$

The next value as well as its sign has been determined in the experiment of Schmidt et al.(3):

$$e^2_{3x} = 3{,}7.10^{-5} \text{ dyne}^{1/2} \;,\; e^2_{3x} \quad 0 \;. \qquad /3/$$

As we see, despite the diminished K_{33} value for the first case, the difference is one order of magnitude.

The question is: what is the reason for this big difference? Our suggestion is that the explanation of this experimental fact is connected with the different influence of surface polarization (SP).

SURFACE POLARIZATION

Such a polarization arises in general because of the asymmetric action of the interface glass - LC. For the first time phenomenological ideas for the asymmetry of the interface air - LC have been developed in (4). We noticed that the sign of the surface asymmetry could be different depending on the specificity in surface interactions. A comparison of the ways for producing homeotropic orientation in the experiments, mentioned above shows the following: At the first experiment a polyamide resin doping was used and the glass surfaces were clean. At the second experiment however they were lecithin coated.

An analogy with lyotropics leads us to the following concept: The MBBA molecule, which two ends differ in their hydrophility will be preferentially oriented towards the clean glass substrate with its hydrophilic end - the polar methoxy group OCH_3, while towards a lecithin treated - with its hydrophobic tail C_4H_9. Then the longitudinal dipoles of most of the molecules in the surface layer will be preferentially oriented and the direction of this orientation for the two cases considered will be just the opposite.

The value of the SP is given by the formula

$$m_p = n\, x_p\, \mu_\parallel \qquad /4/$$

where n - number of molecules per unit area,

$x_p = (n\uparrow - n\downarrow)/(n\uparrow + n\downarrow)$ - the relative number of oriented molecules, in general position dependent, and

$\mu_\parallel$-longitudinal dipole moment .

Let us make an estimation: At a cross section area area of MBBA molecule equal to 50 Å^2 one gets $n = 2.10^{14}$ molecules.cm^{-2}. Then taking $\mu_\parallel = 0{,}75$ debye for MBBA (5) and for x_p its maximal value $x_p = 1$, one obtains

$$m_p = 1{,}5.10^{-4}\,\text{statcoul.cm}^{-1} = 1{,}5.10^{-4}\,\text{dyne}^{1/2}; \qquad /5/$$

which is four times greater than the e_{3x} value, measured in the second experiment.

SP could be considerably increased if the asymmetric action of the wall penetrates deeply in the layer volume. Similar assumptions can be found in (6). Let's estimate the possible penetration depth. If we take for it the distance up to what a molecule piking up from the surface 'forgets' its initial orientation we will have

$$a = \sqrt{2\, D_\parallel\, \tau_\perp} \qquad /6/$$

where $\tau_\perp$ - the reorientation time around the transverse molecular axis, $D_\parallel$ - longitudinal diffusion coefficient. For MBBA with $\tau_{\perp} = 10^{-6}$ s (7) and $D_{\parallel} = 2,6.10^{-7}$ cm^2.s^{-1} (8) one gets a = 70 Å, which is nearly 3 times greater than the molecular lenght and tell us that the estimation /5/ can be increased several times.

At molecules with equal end groups m_p is probably too small. Too small will be also SP in a homogeneously oriented layer, because the specific interactions, tending to orient the transverse dipole moment component are probably weak and the reorientation around the long axis is fast.

THEORY

Let us consider now the theoretical description of the homeotropic layer deformation in a horizontal homogeneous electric field (EF) under simultaneous action of the flexoeffect and SP.

As one of us has pointed out (9) in a homogeneous EF the flexoeffect creates surface torques only, without volume action. But similar surface torques arise also because of the coupling between EF and SP, which was stressed in (10). The surface torque balance equation in small angle approximation then takes the form

$$\pm K_{33}(d\theta/dz) + C_{1,2}\theta \mp e_{3x}E - m_{p1,2}E = 0\ , \qquad /7/$$

$$z = \pm d/2$$

where C_1 and C_2 - anchoring energies, m_{p1} and m_{p2} - SP for each of the walls, d - the distance between them. These relations play the role of boundary conditions for the equation

$$K_{33}\,(d^2\theta/dz^2) = 0 \quad . \qquad /8/$$

So we obtain the solution ($b_1 = K_{33}/C_1$, $b_2 = K_{33}/C_2$)

$$\theta(z) = \left(e_{3x} + \frac{m_{p1}b_1 - m_{p2}b_2}{b_1 + b_2}\right) \frac{E}{K_{33}} \cdot \frac{z - z_0}{1 + d/(b_1+b_2)}$$

$$z_0 = \frac{b_2 - b_1}{b_1 + b_2}\,\frac{d}{2} - \frac{(b_1 + b_2 + d)(m_{p1} + m_{p2})}{e_{3x}(b_1 + b_2) + m_{p1}b_1 - m_{p2}b_2} \times$$

$$\times \frac{b_1 \, b_2}{b_1 + b_2} \qquad /9/$$

This solution is a generalization of that in (1), where $b_1 = b_2$ and m_p is not taken into account.

Let us assume that the boundary conditions are symmetrical, i.e. $b_1 = b_2$ and $m_{p1} = m_{p2}$. Now we see that the experimentally measured value is not e_{3x} itself but just the sum $e_{3x} + m_p$. Depending on the sign of m_p we can obtain bigger deformation when the two torques act in concert and smaller - in the opposite case. This is just the explanation of the drastic discrepancy mentioned at the beginning.

RESULTS AND CONCLUSION

Following the theory, we can write

$$\begin{aligned} e^1_{3x} &= e_{3x} + x^1_p \, m_{po} \\ e^2_{3x} &= e_{3x} - x^2_p \, m_{po} \end{aligned} \qquad /10/$$

where m_{po} - the maximal possible value of SP (when $x_p = 1$). Taking the treble value of /5/ one gets $m_{po} = 4,5.10^{-4}$ dyne$^{1/2}$. Unfortunately there are three unknown values in the two relations /10/ so that the evaluation of e_{3x} requires some estimation of the difference

$$x^1_p - x^2_p \quad .$$

In general this difference can range from -1 to 1 so that the possible range for e_{3x} is from $-0,7.10^{-4}$ to $3,7.\ 10^{-4}$ dyne$^{1/2}$ with a mean value $1,5.10^{-4}$ dyne$^{1/2}$ corresponding to $x^1_p = x^2_p$.

x_p could be expressed by the Boltzman factor $B = -\Delta E/kT$, where ΔE is the energy difference between the two molecular orientations, as

$$x_p = (1 - \exp B) / (1 + \exp B) \qquad /11/$$

The value of ΔE could be provided by a detailed model of surface - end group interactions to be attempted in the future. Any way, if $\Delta E \sim kT$ both x_p^1 and x_p^2 are smaller than one and their difference cannot exceed two - three tenths. Than the order of magnitude of e_{3x} will be 10^{-4} dyne$^{1/2}$ as well, with a positive sign.

The uncertainty of the estimation is even bigger, having in mind that the sign of the e_{3x}^1 has not been determined in the experiment (2), so that the negative one is also permissible. Still the probable order of magnitude is again 10^{-4}.

Such order of magnitude is more realistic than the broadly assepted value e_{3x}^2. It resolves the apparent contradiction between different experiments, dealing with flexoelectric effects in MBBA.

In conclusion, the aim of this letter is to call for new experiments in this field, because it is evident that the true value of bend flexocoefficient in the case of nematic LC's composed by molecules with different end groups can be evaluated only after carefulcomparison between the results from the experiments with definite hydrophilic and hydrophobic surfaces.

On the other hand such experiments can provide important information about this relatively new aspect of surface interaction in LC's - the surface polarization. The direct coupling between surface polarization and electric field could find some interesting display application as well. There exist few examples of this type in the literature.

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