

Mechanism of homeotropic alignment of a doped liquid crystal

T. BEICA^a, R. MOLDOVAN^b, I. ZGURA^a, S. FRUNZA^a, M. POTERASU^a

^aNational Institute for Materials Physics, PO Box Mg-07, Magurele, R-77125, Romania

^bRomanian Academy Centre of Advanced Studies in Physics, Bucharest, Calea 13 Septembrie no.13, Romania

In the paper, the physico-chemical orientation mechanism on solid surfaces for a liquid crystal (NP5 from Merck) doped for homeotropic alignment, is tested. For that, the dispersion and polar parts of surface tension of the liquid crystal are determined. Using substrates with and without adsorbed surfactant, the dispersion and polar parts of the surface tension of the substrates were also measured. Comparison of liquid and solid surface tensions, involved in the physico-chemical mechanism, failed to explain the difference of the molecular alignment for the two substrates. In the presence of the surfactant adsorbed on the surface, the steric model probably gives the explanation for the homeotropic alignment.

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1. Introduction

Liquid crystal displays require uniform molecular alignment on the glass surfaces for their working. The most important orientational configuration of nematic liquid crystals for obtaining electro-optical effects used to obtain displays are: homeotropic (perpendicular), planar and tilted. Various methods for obtaining uniform alignment have been proposed, but the mechanisms of molecular alignment are not yet well understood. Among the methods for obtaining the homeotropic alignment we mention the treatment of the surfaces with acid, the coverage the surfaces with a very thin layer of lecithin, dimetipolyxiloxane, alcosilan DMOAP and the doping of the liquid crystal with surface agents [1]. The main methods to obtain uniform planar orientation are the unidirectional rubbing of a thin polymeric layer deposited on glass surfaces or the oblique evaporation of a thin dielectric layer (SiO_x) [1]. Mechanical interactions due to surface topology or anisotropy seem to play the role of determining the orientation of molecules in the case of parallel alignment [2]. The physico-chemical interactions such as hydrogen bonding, van der Waals's and dipole-dipole interactions between the liquid crystal molecules and the glass surface is believed to play a dominant role in the orientation of the molecules parallel or perpendicular to the glass surface. A phenomenological hypothesis states that there is a correlation between the anchoring angle of the liquid crystal and the surface tension of the substrate and that low energy substrates produce homeotropic orientation [3]. The correlation between liquid crystal orientation and substrate surface energy components (dispersion and polar) gives a better understanding of the phenomenon [4,5]. In the case of the homeotropic alignment caused by the presence of surfactants there is another model to explain the orientation, namely the steric model that states that perpendicular orientation of surfactant alkyl chains on glass surfaces produces homeotropic orientation of the liquid crystal [6].

The liquid crystal studied in this paper (NP5 from Merck) aligns planar on glass when it is in pure state and homeotropic when a special dopant is added to it. We have checked the correlation between the orientation of the liquid crystal and the components (dispersion and polar) of its surface tension and of the substrate surface energy, testing in this way the physico-chemical orientation mechanism.

2. Theory

The interfacial tension liquid-solid is related to the surface tension of the liquid and phases at the interface with vapours by Young relation [7]. This relation that establishes the mechanical equilibrium between several surface tensions (Fig. 1) is:

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta \quad (1)$$

where the subscripts have the signification: S - solid, L - liquid, V - vapour, and θ is the contact angle. Among these quantities, γ_{LV} and $\cos \theta$ are measurable and the surface tensions of the solid can be calculated.

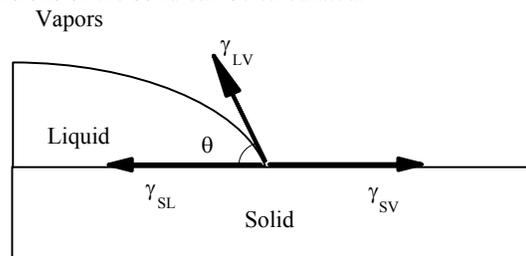


Fig. 1. Equilibrium of a liquid drop on a solid surface

Mainly two types of molecular interactions produce the surface energy: dispersion and dipole-dipole (polar). Considering that these contributions are additive:

$$\gamma_L = \gamma_L^d + \gamma_L^p \quad (2)$$

$$\gamma_S = \gamma_S^d + \gamma_S^p \quad (3)$$

where the superscripts d and p represent the dispersion and polar contribution, respectively. In equations (2) and (3) we simplified the notation, writing L instead of LV and S instead of SV.

Introducing the adhesion work, W_a equal to the work necessary to separate the liquid from the solid in contact, on unit area, we have:

$$W_a = \gamma_S + \gamma_L - \gamma_{SL}. \quad (4)$$

On the other hand, considering that the work of adhesion is made up from dispersion and polar contributions each of them expressed as the geometrical mean of dispersion and polar contributions to surface tension [8] we have:

$$W_a = 2\sqrt{\gamma_S^d \gamma_L^d} + 2\sqrt{\gamma_S^p \gamma_L^p}, \quad (5)$$

and we obtain from equation (4):

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\sqrt{\gamma_S^d \gamma_L^d} - 2\sqrt{\gamma_S^p \gamma_L^p}. \quad (6)$$

Introducing γ_{SL} , given by eq. (6), in Young equation (1) we obtain:

$$\frac{\gamma_L(1 + \cos \theta)}{2} = \sqrt{\gamma_S^d \gamma_L^d} + \sqrt{\gamma_S^p \gamma_L^p}. \quad (7)$$

Equation (7) allows determining γ_S^d and γ_S^p from contact angle measurements for liquids with known γ_L^d and γ_L^p .

We note that equation (6) holds also for the contact between two immiscible liquids denoted 1 and 2 [8]:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1^d \gamma_2^d} - 2\sqrt{\gamma_1^p \gamma_2^p}. \quad (8)$$

For liquid crystals, the equilibrium value of surface tension depends on the anchoring angle α of the liquid crystal director with the normal to the free surface:

$$\gamma_L = \gamma_L(\alpha). \quad (9)$$

In this case, equation (6) has the form [4]:

$$\gamma_{SL}(\alpha) = \gamma_S + \gamma_L(\alpha) - 2\sqrt{\gamma_S^d \gamma_L^d(\alpha)} - 2\sqrt{\gamma_S^p \gamma_L^p(\alpha)}. \quad (10)$$

In the simplified hypothesis of an identical orientation of the liquid crystal at the solid substrate and at the free surface, the equilibrium orientation of the director at the solid substrate is given by minimizing the interfacial tension:

$$\frac{\partial \gamma_{LS}(\alpha)}{\partial \alpha} = 0. \quad (11)$$

Following Parson [9]:

$$\gamma_L(\alpha) = \gamma_{\perp} + \Delta\gamma \sin^2 \alpha \quad (12)$$

where $\Delta\gamma = \gamma_{\parallel} - \gamma_{\perp}$ and the subscripts refer to parallel and perpendicular to the surface, we introduce the anisotropies of the surface tension components:

$$\gamma_L^d = \gamma_{L0}^d + \Delta\gamma^d \sin^2 \alpha \quad (13)$$

$$\gamma_L^p = \gamma_{L0}^p + \Delta\gamma^p \sin^2 \alpha. \quad (14)$$

Here γ_{L0}^d and γ_{L0}^p are the experimental components

of the surface tension for a liquid crystal with homeotropic alignment at the free surface. As the surface tension anisotropies are small, admit $\Delta\gamma^d \equiv \Delta\gamma^p \equiv \Delta\gamma$ and also $\Delta\gamma > 0$. The calculations give:

$$\frac{\partial \gamma_{LS}}{\partial \alpha} = \Delta\gamma \left(2 - \sqrt{\frac{\gamma_S^d}{\gamma_{L0}^d}} - \sqrt{\frac{\gamma_S^p}{\gamma_{L0}^p}} \right) \sin 2\alpha = 0. \quad (15)$$

Equation (15) has two solutions: $\alpha=0$ (homeotropic alignment) and $\alpha=\pi/2$ (planar alignment). The planar alignment is stable for:

$$\left(\sqrt{\gamma_S^d / \gamma_{L0}^d} + \sqrt{\gamma_S^p / \gamma_{L0}^p} \right) > 2 \quad (16)$$

and vice versa for the homeotropic alignment.

3. Experimental

The experiments were performed on the liquid crystals NP5 and NP5A (from Merck) the last one being NP5 doped with 0.1% by weight with the surface agent ZLI 584. NP5 is a eutectic mixture of azoxy compounds with nematic domain $-5^{\circ} \dots +75^{\circ} \text{C}$ and negative dielectric anisotropy ($\Delta\epsilon = -0.2$) used for DAP effect applications. ZLI 584 is a carboxylic acid with structure of liquid crystal.

The liquid materials were used without supplementary purification.

In sandwich type cells with untreated glass walls, NP5 gives degenerated planar alignment, while NP5A gives homeotropic alignment. The alignments were stable in the entire nematic domain.

The glass used in experiments was calco-sodic glass cleaned with detergent and rinsed with mono and bi distilled water.

Measurements of surface tensions for NP5 and NP5A were performed using the pendant drop method, a static method adequate for liquid crystals and described in previous papers [10,11]. The method consists in taking images of a steady drop formed at the planar and horizontal end of a circular capillary tube with sharp edges. The images were taken by a digital capture system with a Kodak Megaplug Camera, Model ES 1.0. A Pascal code written by us processed the data, finding the outline of the drop image.

The drop was enclosed in an airtight chamber. The temperature of the chamber was either continuously varied with the constant rate of $0.1^{\circ}/\text{min.}$, or by steps of 1°C . The ratio of the surface tension to density (γ/ρ) was computed in the first case every 1.5 minutes, from the shape of the drop.

The temperature dependence of the density (ρ) of NP5, needed for the determination of the surface tension, was performed using a dilatometer having a capillary tube. The length of the liquid column in the calibrated capillary was measured using an Abbe comparing microscope (Zeiss) with an accuracy of $\pm 1\mu\text{m}$. The dilatometer was introduced in a micro-chamber for temperature control. This one was achieved using TB-150-type device (VEB MLW Profgerade-Werk, Medingen) circulating water

within the micro-chamber walls. The stability of the temperature was $\pm 0.01^\circ\text{C}$. The absolute value of the density at 33.5°C was determined by weighing with the precision of $\pm 1 \cdot 10^{-4}$ g.

We obtained for the temperature dependence of the density (in g/cm^3):

$$\rho = 1.1508 - 8.0579 \cdot 10^{-4} T \text{ (}^\circ\text{C)}.$$

The measurements of interfacial tension of NP5 liquid crystal at the boundary with water were also performed by the pendant drop method. The drop was formed in a quartz cuvette filled with triple distilled water. In this case, the temperature was varied in steps of 1°C .

The values of water densities in function of temperature were taken from literature [12].

The determination of dispersion and polar parts of a solid substrate surface tension was made by measuring contact angles between that solid surface and liquids having known dispersion and polar parts of surface tension. Three liquids were used: water, di-iodmetan and formamide. Two solid surfaces were studied: glass and glass covered with surfactant ZLI 584. ZLI 584 deposition on the glass surface was obtained by dipping in a solution (0.1wt %) in acetone. The results are given in Table 1.

The measurements of contact angles of liquid crystal drops on solid substrate, was performed by directly viewing the drop contour with the same system of taking images, previously described. The liquid crystal drops on glass were formed at the end of a needle of a calibrated syringe, with controlled advance, using a micrometric screw. After the drop formation, the needle was kept inside the drop. In this way advancing or retracting angles could be measured. The profile of the drop end (right and left) was fitted with a second-degree polynomial. The first order derivatives at the contour ends of the drop give the left and right contact angles. The maximum value of the contact angle, obtained immediately after the drop advancing was considered as being the advancing angle. Several determinations were made on the same drop by increasing its volume. The measurements were made at room temperature.

4. Results and discussion

The measurements of surface tension for NP5 and NP5A in the temperature range $18\text{--}50^\circ\text{C}$ show that the

surface tension of NP5 is practically unchanged after doping with the surface agent. Some experimental results for surface tension are given in Fig. 2. From this figure we can observe that the experimental points for surface tension of NP5 and NP5A are placed on the same curve describing the temperature dependence (in the limit of experimental errors), in the temperature range $18\text{--}30^\circ\text{C}$. This behaviour shows that the surface agent is not tensioactive for the liquid crystal NP5, and that its concentration in the superficial layer is near to that in the bulk. On the contrary, the surface agent is probably adsorbed on the glass surface.

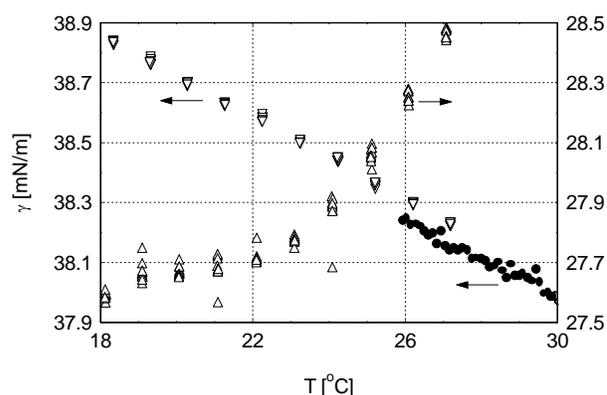


Fig. 2. Interfacial tension (γ) of NP5 and NP5A as function of temperature (T): ∇ - NP5/air; \bullet - NP5A/air; Δ - NP5/water.

The results for contact angle determination for glass (S_1) and glass covered with surfactant ZLI 584 (S_2) are given in Table 1. The values of contact angle θ in Table 1 are advancing angles obtained as a mean value from 3-4 independent determinations.

The dispersion and polar components of glass (S_1) and glass covered with ZLI 584 (S_2) were determined using equation (7) and the least-squares method. We obtained for glass the values: $\gamma_{S_1}^d = 39.9$ dyne/cm and $\gamma_{S_1}^p = 27.6$ dyne/cm. For the glass covered with ZLI 584 we got: $\gamma_{S_2}^d = 40.3$ dyne/cm and $\gamma_{S_2}^p = 28.9$ dyne/cm.

Table 1. Contact angles of three liquids on glass (θ_1) and glass covered with surfactant ZLI 584 (θ_2)

Liquid	γ_L (dyne/cm) Ref.[11]	γ_L^d (dyne/cm) Ref. [11]	γ_L^p (dyne/cm) Ref.[11]	θ_1 (degrees)	θ_2 (degrees)
Di-Iodmetan	51	51	0	29	26
Formamide	58.4	32.4	27	4	3
Water	72.8	21.8	51	25	18

The dispersion and polar components of surface tension of NP 5 liquid crystal (denoted γ_{L0}^d and γ_{L0}^p in equations 13 - 16) were determined using eq. (8) applied

to the interfacial tension between NP5 and water. In the calculations we used the known surface tension of water (component 1) at 20°C , $\gamma_{water} \equiv \gamma_1 = 72.8$ mN/m and its

dispersion and polar parts, $\gamma_1^d = 21.8$ mN/m, $\gamma_1^p = 51.0$ mN/m [13]. We determined at the same temperature the surface tension of NP5 liquid crystal (see Figure 2) $\gamma_{L0} = \gamma_2 = 38.7$ mN/m and the interfacial tension at the boundary between the liquid crystal and water, $\gamma_{12} = 27.7$ mN/m. Solving eq. (8) we obtained for the liquid crystal $\gamma_2^d = \gamma_{L0}^d = 34.6$ mN/m and $\gamma_2^p = \gamma_{L0}^p = 4.1$ mN/m. Equations (13, 14) are valid in the case of studied liquid crystals as observations in polarized light between crossed polarizers on liquid crystal drops on glass show that the orientation at the free surface is homeotropic.

Simple calculations show that for both surfaces (glass and glass covered with ZLI 584) equation (16) holds, so that the alignment should be planar on both surfaces. In this manner the physico-chemical theory can explain the liquid crystal alignment on glass, but not that on glass covered with surfactant. In the latter case, the steric model probably gives the explanation for the homeotropic alignment.

5. Conclusions

The physico-chemical mechanism for the homeotropic alignment of a liquid crystal (NP5 from Merck) by its doping with a surface agent (ZLI 587 from Merck) was tested. For that, we determined the surface tension of the liquid crystal and of the liquid crystal doped with surface agent and also the dispersion and polar parts of the surface tension of the liquid crystal and those of the solid substrate in the absence and presence of a thin layer of the deposited surfactant.

Doping the liquid crystal with the surface agent ZLI 584 its surface tension is not modified, meaning that this one is not adsorbed at the free surface of the liquid crystal. To explain the crucial influence of the doping on the liquid crystal alignment on glass, we suppose that the dopant is adsorbed on the solid surface from the solution. Yet, by covering the glass surface with a thin layer of deposited surfactant we obtained that its surface tension is only slightly modified. So, we conclude that the physico-chemical mechanism failed to explain the alignment of the studied liquid crystal on the glass surface in the presence of the dopant. It is probable that the homeotropic orientation of the liquid crystal molecules is due to the homeotropic orientation of the surfactant alkyl chains and that the steric model explains the homeotropic alignment.

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*Corresponding author: rodi@infim.ro

The typical structure of a liquid crystal device. The pretilt angle of an LCD is either near zero degrees or 90 degrees for using the conventional homogeneous and homeotropic PI materials, respectively. The technique of producing homogeneous and homeotropic PI is mature in the LCDs industry. For example, the introduction of long alkyl groups into the aromatic diamines has been applied for increasing the pretilt angle from near zero degrees to near 90 degrees (Tsuda, 2011). The PAEs of the homogeneous PI alignment layer doped with different POSS concentration and the homeotropic PI alignment layer irradiated with different UV dosage are shown in Fig. 11 and Fig. 12, respectively.