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## Liquid Crystals

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# Self-screening of Langmuir–Blodgett films by a discotic micellar lyotropic liquid crystal

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The influence of the surface treatment on the anisotropic part of the surface tension of a lyotropic discotic micellar nematic liquid crystal doped with ferrofluid is analysed. The treatment involves Langmuir–Blodgett (LB) films deposited on the glass substrates. Textural observations and phase-shift measurements of the transmitted light were carried out. A phenomenological model which allows calculation of the director average orientation in the bulk and at the surfaces is used for interpreting the experimental data. Our results show that the average director alignment depends on the concentration of the magnetic grains of ferrofluid at the glass surfaces. On the contrary, it is practically independent of the nature of the molecule deposited on the glass substrate. According to the model, the flat glass surface, independently of the treatment or the absence of any treatment, stabilizes onto itself a lamellar layer (or bilayer) formed by the amphiphilic molecules of the liquid crystal. This layer screens the effect of the LB film (or of the pure untreated substrate) on the alignment of the lyotropic nematic mesophase.

## 1. Introduction

The average surface orientation of thermotropic liquid crystal molecules strongly depends on the chemical composition of the surface with which they are in contact. This effect can be easily understood in terms of anisotropic van der Waals interactions between the molecules of the mesophase and those of the substrate. According to this point of view, the anisotropic part of the surface tension, responsible for the surface orientation, depends on the dielectric properties of the two media: the liquid crystal and the solid substrate [1]. Jerome and Shen [2] showed that by covering an isotropic glass with different surfactants, different alignments of thermotropic nematic liquid crystals were obtained. An analysis of this kind for lyotropic liquid crystals is to our knowledge absent until now.

In 1991 Oliveira *et al.* [3] observed a gliding director anchoring of calamitic micellar lyotropic nematic liquid crystals on amorphous untreated glass surfaces. In that paper, the dynamical response of the calamitic liquid crystal to the action of a magnetic field was investigated. The experimental results were explained assuming the existence of an amphiphilic bilayer (as in the case of a

lamellar structure) stabilized by the glass surface. To interpret the planar orientation observed in calamitic micellar lyotropic nematics [3], the concept of adhesion could be used [4]. Moreover, in the case studied by the previous authors, in principle there is no easy direction (defined as the one along which the nematic director is aligned, in the absence of a bulk distortion). Instead, there is only an easy plane, since there is an azimuthal degeneration at the cell walls, due to the bilayer symmetry. The experimental investigation with calamitic lyotropic nematics subjected to a magnetic field showed indeed that the local easy direction can glide, rotating under the action of the field [3].

In the present paper we report on experimental data obtained with discotic micellar lyotropic (and in some control measurements, with thermotropic) nematic liquid crystals in contact with various substrates. The surface treatment employed Langmuir–Blodgett (LB) films of different molecules deposited onto the glass plates. The lyotropic liquid crystal used was doped with ferrofluid [5] in small concentrations; the ferrofluid grains migrate to the surface, due to the application of a static magnetic field, exhibiting a field gradient. Thus, the ferromagnetic grains become localized at the surface and, being oriented by the same magnetic field, drive the nematic director alignment in the bulk.

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Recently we have shown that in a system of this kind, the anisotropic part of the surface tension strongly depends on the anchoring strength and on the surface-like splay–bend elastic constant  $k_{13}$  [6], both of which are determined by the sub-surface conditions ( $k_{13}$  is also affected by the material properties). The aim of the present paper is to show that the surface orientation of the discotic micellar lyotropic nematic liquid crystal is practically independent of the surface treatment. According to our point of view it is connected with the presence of a lamellar layer (or bilayer) stabilized by the flat isotropic glass substrate. As a consequence, the surface orientation is independent also of the LB film deposition.

With this purpose, we investigated the role of the substrate treatment on the orientation of lyotropic discotic micellar—and thermotropic—nematic liquid crystals. The experimental techniques used were: polarizing light microscopy (texture investigations and transmitted light measurements) and interferometry. The textures of the lyotropic and thermotropic mesophases were observed, and the bulk tilt angles measured, for cells of lyotropic liquid crystals having different surface conditions, obtained by changing the concentration of ferrofluid doping and the type of molecule and the thickness of the LB film.

## 2. Experimental

The discotic micellar lyotropic nematic mixture (*I*N) investigated had the following concentrations by weight %: decylammonium chloride 41.54;  $\text{NH}_4\text{Cl}$  4.23 and  $\text{H}_2\text{O}$  54.23. The thermotropic nematic (*t*N) material used was 4-heptylcyanobiphenyl K21‡. The *I*N system exhibits the following phase sequence as a function of temperature: L ( $T_{\text{LN}} = 24.8^\circ\text{C}$ )  $\text{N}_\text{D}$  ( $T_{\text{NI}} = 44.0^\circ\text{C}$ ) I, where L,  $\text{N}_\text{D}$  and I are the lamellar, discotic micellar nematic and isotropic phases, respectively. The thermotropic nematogen, *t*N, has the phase sequence Cr ( $T_{\text{CN}} = 30^\circ\text{C}$ )  $\text{N}_\text{C}$  ( $T_{\text{NI}} = 43^\circ\text{C}$ ) I, where  $\text{N}_\text{C}$  and Cr are the calamitic nematic and crystal phases, respectively.

The LB films were deposited onto the glass substrates by means of a KSV5000 apparatus mounted in a clean room (class  $10^{-4}$ ). Three types of substances were used: lignin, cadmium stearate and behenic acid, with various numbers of layers. Lignin monolayers were prepared from tetrahydrofuran extracts of sugar cane bagasse. The lignin was extracted according to the procedures described by Constantino *et al.* [7], and then transferred onto the substrate in the form of Y-type LB films. A detailed account of the experimental procedures adopted is given elsewhere [7, 8]. The behenic and cadmium

stearate depositions were made following the usual procedures [8].

For the experiments concerning texture observations, the liquid crystal material was placed as a droplet on a glass surface, either treated or untreated, and a cover glass was put onto the droplet in the following way, without pressing. The cover glass was positioned along one of the borders of the other substrate and then it was gently lowered onto the droplet to promote a preferential flow direction during the filling procedure. The typical sample thickness obtained was of the order of  $10\ \mu\text{m}$ .

The samples were observed using a Leitz polarizing microscope equipped with crossed polarizers and an INSTEC hot stage. The temperature could be stabilized with an accuracy of  $0.5^\circ\text{C}$ . The rotatory stage of the microscope allowed observation of the textures and measurement of the optical transmittance as a function of the relative orientation of the sample holder with respect to the polarizing direction ( $\theta$ ). The transmittance of the sample averaged over  $0.25\ \text{mm}^2$  was detected by a photodiode placed in the microscope head.

For the measurement of the bulk and effective surface tilt angles ( $\phi_\text{b}$  and  $\phi_\text{e}$ , taken with respect to the normal to the glass plates)§ of the *I*N sample, a small quantity of water-based ferrofluid ( $1\ \mu\text{l ml}^{-1}$ ) was added to the mixture. The typical size of the magnetic grains ( $\text{Fe}_3\text{O}_4$  grains coated with a thin film of oleic acid) was  $100\ \text{Å}$ , and their concentration was typically of the order of  $10^8\ \text{grains cm}^{-3}$ . This concentration is of the same order as the minimum ferrofluid concentration required to produce a collective behaviour of *I*N in the presence of a small magnetic field [9, 10]. At this small concentration we observed that the transition temperatures were not affected by the presence of the ferrofluid [11]. On the other hand, it has to be noted that ferrofluid doping of a *t*N is a very difficult task, because usually the two systems are not mutually soluble. Hence, a homogeneous mixture of ferrofluid and *t*N could not be obtained and for this reason, we do not investigate *t*N doped with ferrofluid in the present work. The *I*N cells mounted in the sample holders had the following sizes: 10 mm width, 25 mm length, and  $d = 500\ \mu\text{m}$  thickness. The filling process of the *I*N cell, with the aim of achieving a homeotropic alignment, involved heating the *I*N to  $30^\circ\text{C}$ ; after that, *I*N was introduced into the cell by gravity, and the sample kept undisturbed for about 1 h at  $30^\circ\text{C}$ . In this way, the homeotropic alignment was obtained.

§We stress the fact that in speaking about ‘surface tilt angle’, we mean the tilt angle at the interface between the bulk and a subsurface layer ( $\sim 100\ \text{Å}$ ), as viewed from the side of the bulk; hence, we are able to apply continuum theory for the calculation of both  $\phi_\text{b}$  and  $\phi_\text{e}$ .

‡K21 was synthesized by C. Germain, Laboratoire de Physique des Solides, Orsay, France.

The sample was placed in a temperature controlled device (accuracy within  $0.05^\circ\text{C}$ ), in the presence of a non-homogeneous magnetic field  $\mathbf{H}$  applied at an angle  $\phi_H = 60^\circ$  with respect to the normal to the  $tN$  slab ( $H_{\max} = 400\text{ G}$ ). The field was produced by two permanent magnets placed symmetrically from the centre of the sample. The experimental set-up is described in more detail elsewhere [6, 12]. Due to the application of the non-homogeneous magnetic field, the coupling between the field gradient and the magnetic moments of the grains displaced the grains from the sample centre towards the glass walls. At equilibrium, there were no longer any magnetic grains in the bulk; all had moved to the surface. The typical surface density of the magnetic grains was of the order  $10^6\text{ grains cm}^{-2}$ , which corresponds to an average distance among them of a few microns.

The  $N_D$  phase investigated has a negative diamagnetic anisotropy. Hence, in the presence of  $\mathbf{H}$ , the director  $\mathbf{n}$  tends to be oriented perpendicularly with respect to the field itself [13]. The measurements of the optical path difference were made using a Leitz microscope with a Berek tilt compensator. To minimize experimental errors, a set of five independent measurements was made at each temperature, and a mean value calculated.

### 3. Results and discussion

#### 3.1. Textures and transmittance measurements of $tN$ and $iN$

The typical light transmittance (between crossed polarizers) through the  $tN$  liquid crystal K21 was measured versus the polarizing angle  $\theta$  with treated (eight layers of behenic acid or six layers of cadmium stearate) and non-treated glass surfaces. In the case of samples placed between treated cell substrates the transmittance exhibited a very small value practically independent of  $\theta$  (variation of about 10%), indicating that the nematic director  $\mathbf{n}$  had on average a preferred homeotropic alignment, i.e. normal to the treated glass surface. In the case of the non-treated glass, the light transmittance showed a strong  $\theta$  dependence, varying by a factor of three from the minimum to the maximum values. This indicates the planar alignment of  $tN$ .

However, in the case of  $iN$  cells the light transmittance was higher than for the  $tN$  treated cells. Moreover, it was practically independent of  $\theta$  for both treated and non-treated substrates: the variation observed in the transmittance was less than 5% in all situations. This fact indicates that in both cases the nematic director does not show a preferred orientation.

The texture observations on  $tN$  confirm previous conclusions. In particular, in the case of treated glass

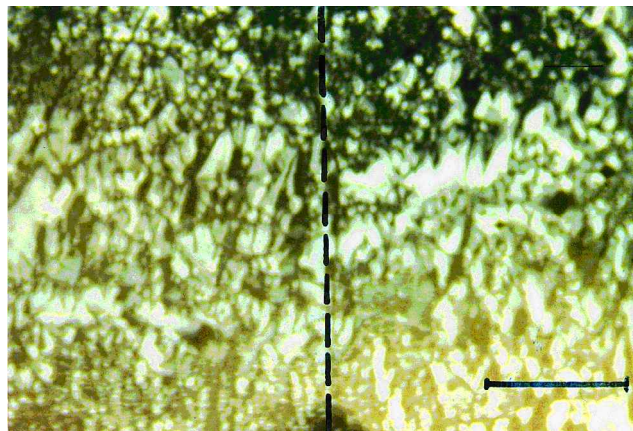


Figure 1. Typical schlieren texture of a lyotropic nematic sample on treated (6 cadmium stearate LB layers) and untreated glass surfaces. Optical microscopy observation between crossed polarizers; the segment length is  $340\mu\text{m}$ . The dashed line divides the treated (left side) from the untreated (right side) region of the glass surfaces; temperature  $30^\circ\text{C}$ .

surfaces many small domains appeared, presenting interference colours (nematic marble texture with disclinations [14]). This indicates that the director orientation was in fact only quasi-homeotropic, being characterized by a partial azimuthal degeneracy, and so lying at the surface of a cone whose axis is perpendicular to the glass surface. Instead, the  $tN$  sample in non-treated glass cells showed a preferential unidirectional planar texture with many defects. The reason for such an alignment is related to liquid crystal flow during cell filling [15].

On the other hand, the  $iN$  sample placed between both treated and non-treated surfaces presented the same schlieren texture (figure 1). This figure is particularly illustrative of the phenomenon, because the dashed line divides the treated (left side) from the non-treated (right side) regions of the cell, with which the  $iN$  material is in contact. The textures have the same features on both sides. This confirms the average non-preferential alignment of  $\mathbf{n}$ , both in the presence and in the absence of any particular treatment.

These results remain valid for all the LB films investigated in the present work. In conclusion, the LB deposit strongly affects the alignment of the  $tN$  director, whereas no detectable difference was observed for  $iN$  samples in contact with both treated and non-treated cell substrates.

#### 3.2. Measurements of the tilt angles in $iN$

To investigate in more detail the bulk and surface tilt angles of  $\mathbf{n}$  in the  $iN$  liquid crystals, the optical path difference was measured as a function of the temperature under various experimental conditions.

### 3.2.1. Different ferrofluid concentrations

Two ferrofluid doping concentrations were used:  $c_1 = 0.96 \times 10^8$  grains  $\text{cm}^{-3}$  and  $c_2 = 4.76 \times 10^8$  grains  $\text{cm}^{-3}$ .

In the limit of small birefringence, the bulk tilt angle ( $\phi_b$ ) can be calculated, using the measured optical path difference  $\Delta$ , according to the expression [12, 16]

$$\Delta = \frac{R n_o d}{2} \phi_b^2 \quad (1)$$

where  $R = 1 - (n_o/n_e)^2 \ll 1$  for normal *IN* materials,  $n_e$  and  $n_o$  being the extraordinary and ordinary refractive indices [17], respectively. The values of  $\phi_b$  as a function of temperature for the *IN* samples with both ferrofluid concentrations are shown in figure 2. The experimental deviations in  $\phi_b$  are about 0.01 rad. The glasses used in these sample cells were not treated with any LB deposit. The only difference between the experiments is the concentration of ferrofluid grains at the glass surfaces. The samples with the greater concentration of grains showed a systematically larger value of  $\phi_b$ .

To calculate the tilt angle of the director at the surface,  $\phi_e$ , we used a phenomenological generalization [12] of the thermodynamical model proposed by Fontanini and co-workers in 1996 [6]. This extension takes into account the different contributions to the surface energy of the residual lamellar layer and of the ferrofluid grains. In the framework of this model,  $\phi_b$  and  $\phi_e$  are written

as:

$$\phi_e(T) = \frac{(\pi/2) - \phi_H}{1 + A'/(T - T_{NL})^2} \quad (2)$$

$$\phi_b(T) = \phi_e(T) - \frac{1}{2} \left[ \frac{T_o^{1/2}}{\delta(T_o - T)^{1/2}} A + B \right] \sin 2\phi_e \quad (3)$$

where  $\delta$  is a constant (evaluated as 0.858 for this lyotropic mixture [17]), and  $A$ ,  $A'$  and  $B$  are the fitting parameters of the model. Note that  $T_{NL}$  is the critical temperature for the  $N_D$ - $L$  phase transition, while  $T_o$  is a temperature a little bit higher (about 1°C) than  $T_{NL}$ . The strategy to calculate  $\phi_e$  is the following: equation (2) must be substituted into (3); the expression obtained is then used to fit the experimental values of  $\phi_b$ , and in this way the parameters  $A$ ,  $A'$  and  $B$  are found.  $A'$  is then introduced in equation (2) in order to obtain  $\phi_e(T)$ . A detailed description of the fitting procedure and of the fitting sensitivity with respect to the choice of parameters is discussed elsewhere [12]. These results, in the case of the two different ferrofluid concentrations, are reported in figure 3. The values of  $\phi_e$  for both samples tend to  $(\pi/2) - \phi_H$  when  $T$  approaches  $T_o$ , since  $\mathbf{n}$  tends to align normally with respect to  $\mathbf{H}$ . Note that the degeneracy of  $\mathbf{n}$  around  $\mathbf{H}$  is broken by the presence of the surface. When  $T$  decreases towards  $T_{NL}$ ,  $\phi_e$  also decreases in both samples. This process is more accentuated in the sample with the larger ferrofluid concentration.

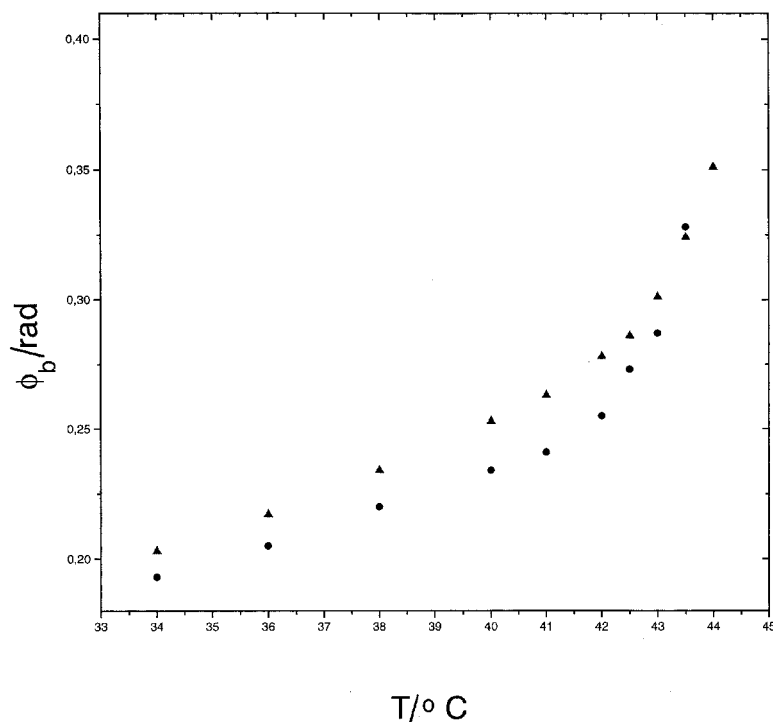


Figure 2. Bulk tilt angle  $\phi_b$  as a function of temperature  $T$ . Lyotropic nematic samples doped with ferrofluid at different concentrations of grains. ●  $0.96 \times 10^8$  grains  $\text{cm}^{-3}$ ; ▲  $4.76 \times 10^8$  grains  $\text{cm}^{-3}$ .

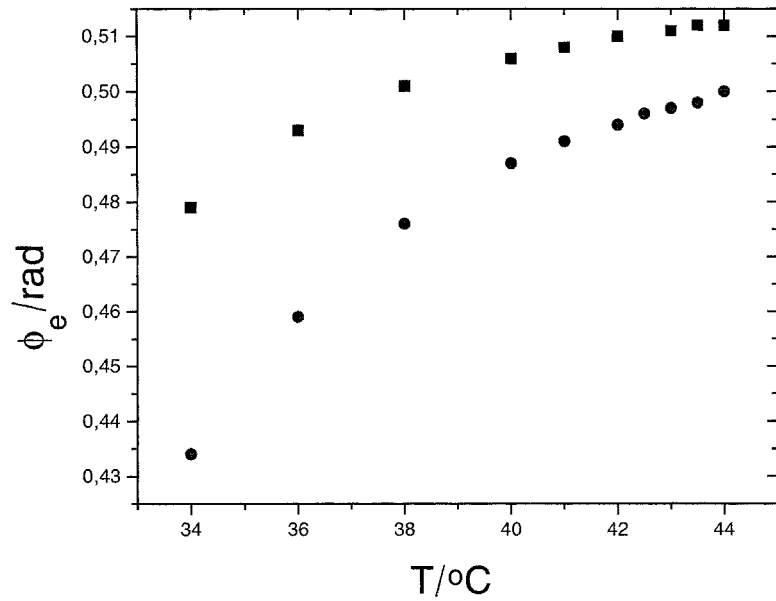


Figure 3. Surface tilt angle  $\phi_e$  as a function of temperature  $T$ , according to the model. Lyotropic nematic samples doped with ferrofluid at different concentrations of grains ■  $0.96 \times 10^8$  grains  $\text{cm}^{-3}$ ; ●  $4.76 \times 10^8$  grains  $\text{cm}^{-3}$ .

As expected, the sample with the larger ferrofluid concentration exhibits a smaller surface tilt angle  $\phi_e$ .

In conclusion, through these experiments, we realize that the ferrofluid doping modifies the properties of the glass–liquid crystal interface. The tilt angles at the surfaces and in the bulk are dependent on the doping, and our present results confirm those reported recently [12].

### 3.2.2. Different LB deposited films

A set of samples was analysed:  $S_1$  and  $S_2$  had one and five layers of lignin, respectively;  $S_3$ ,  $S_4$ ,  $S_5$  had four, five and six layers of behenic acid, respectively;  $S_6$ , on the contrary, was not treated. All the samples contained the same amount of ferrofluid grains. The experimental set

up was the same as that used in the previous experiment and, as stressed above, the field gradient removed the magnetic grains from the bulk, transferring them to the cell surfaces. This fact was verified by measuring the critical field for the usual Fréedericksz transition [18], which was found to be 2000 G. Figure 4 shows the experimental results for  $\phi_b$ , calculated by applying equation (1), as a function of temperature for the set of samples under consideration. Inspection of these results indicates that, within the accuracy of the experiment (about 0.01 rad), the bulk tilt angle  $\phi_b$  is independent of the surface treatment.

We stress that this conclusion follows directly from the experimental data for the optical path difference,

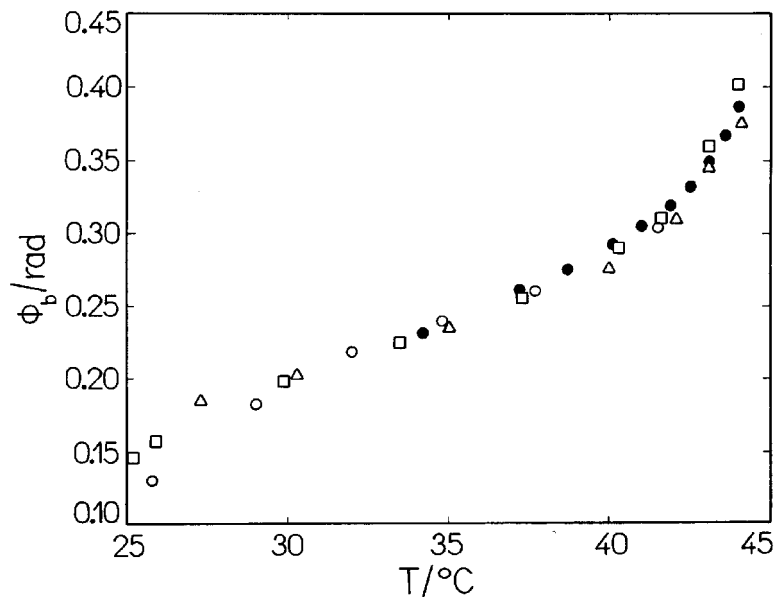


Figure 4. Bulk tilt angle  $\phi_b$  as a function of temperature  $T$ . Lyotropic nematic samples on treated and untreated glass surfaces. □ Glass treated with 5 LB lignin layers; ● glass treated with 6 LB behenic acid layers; ○ untreated glass; △ glass treated with one LB lignin layer.

without any hypothesis or model concerning the surface interactions. This means that, independently of the mechanism responsible for the surface alignment, the bulk orientation of the  $IN$  director does not depend on the surface treatment. This result is new, and completely different from anything observed with  $iN$  substances. As a consequence, taking into account the model described by equations (2) and (3), *the surface tilt angle  $\phi_e$  also turns out to be independent of the surface treatment.* This result seems to indicate that surface orientation in the case of  $IN$  has only a steric origin.

A possible explanation of these results is that the glass surface (with or without any treatment) stabilizes onto itself a lamellar layer or bilayer) constituted by the amphiphilic molecules of  $IN$ . The  $IN$  micelles essentially *feel* this layer and *not* the glass surface, neither bare nor covered by the LB film. This lamellar layer can be interpreted as a *self-surface treatment*, created by the  $IN$  material itself painting micelles onto the substrate, due to the  $IN$  adhesion. This spontaneous  $IN$  layer seems to screen completely the effect of any possible LB film deposited onto the substrate. Taking into account that in this experiment the LB films used are very different (even and odd numbers of layers, small molecules and macromolecules), we believe that our results are quite general, at least when discotic micellar  $IN$  are considered. This description agrees also with the hypothesis made by Oliveira *et al.* [3], previously introduced to interpret the director gliding of calamitic  $IN$  in the plane of the glass surface.

Let us point out that the  $IN$  systems considered here involve two interfaces in which a lamellar layer or bilayer (created by the  $IN$  molecules), the magnetic grains (coming from the ferrofluid doping), and a possible LB film deposited onto the substrate are competing in trying to orient the  $IN$  micelles. In general the anisotropic part of the surface tension  $\gamma$ , fixing the easy direction, is given by

$$\gamma = \gamma(\text{lamellae}) + \gamma(\text{magnetic grains}) + \gamma(\text{LB}) \quad (4)$$

where the three terms in equation (4) refer to the different interactions. Since the  $IN$  material and the ferrofluid concentrations are the same in all the samples investigated, we conclude that the last term in equation (4) is screened by the lamellar layer. The screening effect cannot be due to the ferrofluid grains, since their surface concentration is too low.

#### 4. Concluding remarks

In conclusion, unlike calamitic thermotropic liquid crystals, lyotropic discotic micelles in a nematic phase are rather insensitive to the LB surface treatment of the solid substrate. There is a form of  $IN$  self-protection from the environment. This protection is explained as being due to the formation of a lamellar layer (or bilayer)

at the interface, which screens the long range van der Waals forces. We believe that this effect is characteristic of the lyotropic nature, irrespective of the particular phase—as the dependency on the surface treatment is characteristic of the thermotropic nature, irrespective of the calamitic or the discotic shape of the molecule. In fact, for the flat substrates considered in the present work, this conclusion seems to be, *a posteriori*, straightforward. It should then be interesting to study different substrate geometries.

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