Optical study of the interface between the lyotropic L_3 (sponge) phase and solid substrate

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Abstract

The interface of the anomalous L_3 (sponge) phase with the solid substrate is studied using elipsometry, total internal reflection and interferometry. The results show the presence of the surface induced layer with the properties different from the properties of the bulk L_3 phase. We conclude that this surface induced layer is the L_α phase.

Keywords: liquid crystal, lyotropic system, sponge L_3 phase, surfactant, reflection ellipsometry, total internal reflection, surface ordering.

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1. Introduction

Recently, the surface properties of thermotropic liquid crystals (LC) have become a matter of much theoretical and experimental attention (see review [1]). On the one hand the interest stems from the practical significance of a solid – liquid crystal interface in the production of liquid crystal displays [2]. But, on the other hand, it is more fundamentally rooted in the fact, that often even in the isotropic phase surface forces lead to novel orientation phenomena, which are essentially unobservable in the bulk. It is well known now that a substrate can induce nematic or smectic ordering near the surface [3-9], while the bulk liquid crystal is still in the isotropic phase. Despite a substantial amount of information, which has been gathered on the bulk properties of the lyotropic liquid crystals, the surface ordering of these mesophases remains scant.

Lyotropic systems are multicomponent solutions and exhibit very rich structural polymorphism. In a lyotropic solution solute molecules are assembled in large aggregates. If the solute is a surfactant, the aggregates are called micelles. The size and shape of the micelles depend on the composition of the system and temperature. The amphiphilic properties of the surfactant molecules often favor the solubility of the admixtures that are insoluble or slightly soluble in a given solvent. The admixture molecules penetrate in the surfactant aggregates and might change their topology. Such an admixture is called a cosurfactant. Depending on the character of ordering of the micelles in a given system the system can be either in a liquid crystal or in an isotropic phase. In contrast to the liquid crystal phases the lyotropic isotropic phases do not have thermotropic analogs. They are complex fluids and have anomalous properties comparing to the conventional isotropic liquids.

The isotropic L_3 phase has a structure of a sponge. The body of the sponge is formed by surfactant bilayers. The bilayers are multiconnected along three directions of space with no long range order. The surfactant molecules in the bilayers form a two-dimensional liquid [10]. The bilayers separate the solvent to two disconnected equivalent subvolums. The anomalous bulk properties of the L_3 phase such as a flow-birefringence, low viscosity, large electrical resistivity etc. have been intensively studied and are now well understood. Extraordinary surface phenomenon of the epitaxy of the L_3 phase on the interface with the lamellar liquid crystal L_α phase was described in [11]. According to [11] the L_α phase has an oblique anchoring on the interface with L_3 phase. The experimental observations of the L_α - L_3 transition under shear [12] and on heating as well as on cooling [13] are described in current literature. Moreover, the authors of [14] describe the existence of the L_α phase in the L_3 phase cell of the Surface Forces Apparatus. They explain the occurrence of the L_α phase as a result of a phase transition induced by the Surface Forces Apparatus. Also there are no evident interdictions to suppose that this layer spontaneously exists on the interface between the L_3 phase and solid surface even without any external action. In principle, because of the sponge structure of the L_3 phase, the bilayers have to occur on the interface with the substrate at different angles in different points of the interface, implying high anchoring energy cost. Taking into account the instability of the L_3 phase with respect to the transition to the L_α phase under an external action and amphiphilic properties of the surfactant molecules one can expect that a thin L_α phase layer covers the interface of the L_3 phase with a solid substrate.

Our previous experiments show that the organization of the surfactant aggregates of the L_3 phase on the interface with a solid substrate indeed differs from the bulk structure. From the conductivity measurements we have concluded that a smooth solid substrate induces quite thick (about 1 μm) L_α layer on the interface with the L_3 phase [15]. To continue this study we have performed several optical experiments: reflection ellipsometry, total internal reflection (TIR), angle light transmittance (interference) of the L_3 phase cell. Below we present these results.

2. Experiment

The investigated sample. The mixture cetylpyridinium chlorid (CPCl)–hexanol – brine is the lyotropic system under the study. CPCl (surfactant), hexanol (cosurfactant) were obtained from Sigma and used with no further purification. Brine (Normal Saline steril and pyrogen free solution (0.9% NaCl)) was produced by HUMAN Godollo-Budapest, Hungary. The components of the mixture were weighted, introduced in the test tubes, heated, twice stirred and centrifuged. The phase diagram of this system was built in our previous study [16]. The phase state was determined by direct polarized light observation. The brine concentration in the L_3 phase sample is 89%. The cosurfactant (hexanol)-to-surfactant (CPCl) weight ratio (h/c) is 1.20.

2.1. Ellipsometry

Ellipsometry is a well-established nondestructive optical method for the characterization of ultra thin films [17]. It uses the fact that, in general, the state of the polarization changes upon generally. Our experimental set-up is based on a null elipsometer in a PCSA arrangement. Polarizer P and compensator C are used to adjust a desired state of the polarization of the incident beam. The state of the polarization is modified due to the reflection of the interface between the L_3 phase sample S and the right angle prism and subsequently examined by ananalyzer A. A measurement on four-zone averaging eliminates most intrinsic imperfections of the optical components as well as many errors due to misalignments of the ellipsometer. The helium-neon laser light of the wave length 632.8 nm incidences perpendicularly on the prism surface and, hence, occurs on the investigated interface in the incidence angle 45^o. The prism contacts with the solution and hermetically covers the cell of the 5mm gap. Measuring the positions of the polarizer and analizer we obtain the ellipsometrical parameters Δ (a phase shift) and Ψ (an azimuth).

If the investigated sample is isotropic and no surface film is present on the interface, the phase shift is to be zero or 360^o [17]. Indeed, in the control experiment for the measuring cell filled with distilled water we have found Δ=359.89^o. The deviation from the 360^o value is of order of the experimental error. The azimuth ψ is a function of the incidence angle ϕ, the refractive indices of the prizm and studied sample. In our case ϕ =45^o and for the cell with distilled water we're obtained Ψ_w = 8.3^o. For this value of Ψ and previously measured refractive index of the prizm n_{pr} = 1.516 solving the Drude's equations we found refractive indices of distilled water n_w = 1.333. This value is in good agreement with table values [18] and our measurement results in TIR technique, described in the next section.

In contrast to the cell filled with distilled water the cell with the L_3 phase gives:

Δ=357.02^o, Ψ=7.31^o.

Such a value of Δ is not typical for the isotropic uniform substrate. The nonzero (and different from 360^o) value of the phase shift indicates that the surface region of the L_3 phase has a structure different from that of the bulk. To estimate the parameters of the surface region we used the simplest model of a bounded isotropic film covered the investigated interface (L_3 phase). Using the Drude's equation we have obtained the refractive index of the surface region of the L_3 phase sample n_s = 1.352. In the calculations we used the value of the refractive index of the bulk phase n_{L3}= 1.345 obtained with the Abbes refractometer and with the Total internal reflection (TIR) technique. The studied system does not absorb light, and Drude's equation has many solutions for the thickness of the surface film (0.135, 0.52, 0.905μm, …). The difference between the bulk and surface values of the refractive indices implies the difference in the structure of the surface layer and the bulk. The results described in the next section show that refractive indices of the L_α and L_3 phases for the same brine concentration are close: $n_{L\alpha}$ = 1.346 and n_{L3} = 1.345 respectively. Thus, the nonzero difference $\delta n = n_s - n_{L3}$ results from the difference in the brine concentration (read interlamellar distance) near the surface and in the bulk rather than from the difference in the structure of the bilayers. $\delta n>0$ implies that the brine concentration at the surface is lower than in the bulk. Such relation between brine concentrations of the surface layer and bulk L_3 phase is in good agreement with the assumption that the surface layer is the L_α phase. It was shown in [11] that when L_α and L_3 phases are in contact, the equilibrium brine concentration in the L_3 phase part is higher than in the L_α phase.

Therefore, the ellipsometry as well as the conductivity measurements [17] presents an evidence of the existence of the surface induced L_α layer while the bulk is in the L_3 phase. In the next section we describe the results of the direct measurement of the optical anisotropy of the interface of the L_3 phase with a glass prism using TIR technique.

Although it is known that the bulk L_α and L_3 phases have well observed interface, it is not likely to expect that the surface L_α layer has sharp interface with the bulk L_3 phase as well. One can verify measuring the angle dependence of the light transmittance. If the surface layer were a bounded thin film of the thickness of order of the light wavelength with the refractive index different from the refractive indices of the bounding mediums, the corresponding light interference phenomena have to be observed. The results of such experiment are described in the section 2.3.

2.2. Total internal reflection (TIR)

The expected value of the birefringence of the surface layer is of order of the corresponding value for the L_α phase that on the phase diagram is located near the phase boundary with the L_3 phase and has the same brine concentration. Since the optical anisotropy of the L_α phase is very low, it can be roughly estimated at direct observation of the test-tube between the crossed polarizers. The test-tube, filled by the L_α phase, between crossed polarizers displays interference colors of the first order. It is easy to estimate that the birefringence is of order 10^{-5}. It is a quite small value and it is not obvious that one can directly register it by measuring the ordinary and extraordinary indices. Nevertheless there is a little chance that the birefringence of the surface layer is higher than that of the L_α phase if the brine concentration at the surface is much lower than the corresponding bulk value. To verify this possibility we're performed the TIR experiment.

The TIR experiment was done on the computer controlled set-up. The intensity of the laser beam (λ=632.8nm) reflected from the interface between the glass prism and L_3 phase was measured as the function of the incidence angle. The incidence angle was changed by rotation of a mirror with a NEWPORT motorized stage with the step 0.01 angle degree. The studied solution was filled in the cell assembled with a right angle glass prism and glass substrate. The cell was sealed by epoxy glue and mounted on the translation stage. Translating the cell along the perpendicular to the studied interface one can keep the probed point unchanged at changing the incidence angle. To fix the position of the reflected beam on the photodetector one more mirror mounted on the rotating stage was installed between the cell and photodetector.

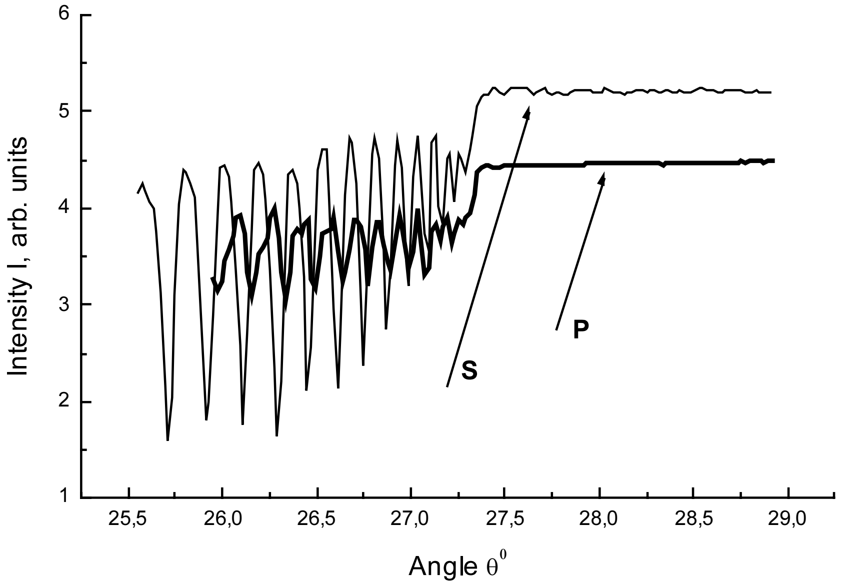

Fig.1. Light intensity as a function of the incidence angle for *s*- and *p*-polarization for the L_α phase. n_o=n_e= 1.346, Δn<0.001, d=25μm.

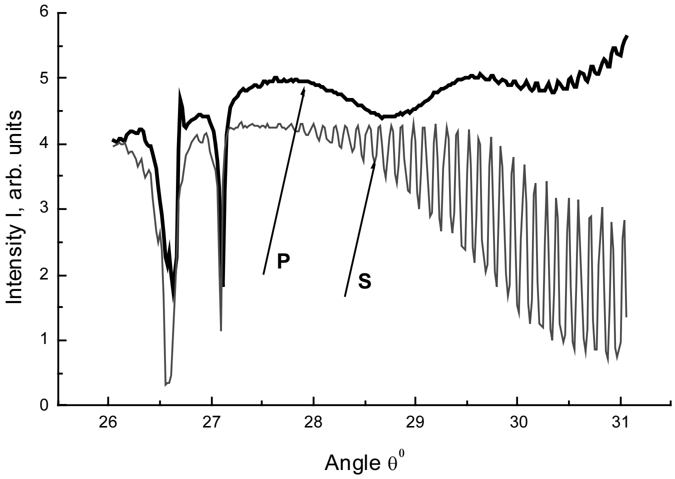

Fig.2. Light intensity as a function of the incidence angle for *s*- and *p*-polarization for the L_3 phase. $n_o=n_e= 1.345$, $d =3.5\mu m$.

We measured the critical angles of the TIR for the L_α phase sample (Φ=89%, h/c=1.10) for *s*- and *p*-polarizations. The results are shown in fig. 1. It turned out that the birefringence of the L_α phase is less than 0.001. The extraordinary and ordinary indices were found to be equal $n_e=n_o=1.346 \pm 0.0005$. For the L_3 phase we obtained $n_e=n_o=1.345 \pm 0.0005$. Thus, the birefringence of the system is too small to study directly the anisotropical effects. It is worth to notice that the total internal reflection from the L_3 phase – solid substrate interface is frustrated at angles higher than the critical angle of TIR. The frustration might be a result of the existence of a thin film on the interface. However, the other mechanisms of the frustration are possible. Future investigations of the Frustrated Total Internal Reflection are needed.

For the comparison with above given results in fig.3 we present the results of the TIR experiment for the cell with brine. The refractive index deduced from this result is n=1.333, i.e. well agreed with [18].

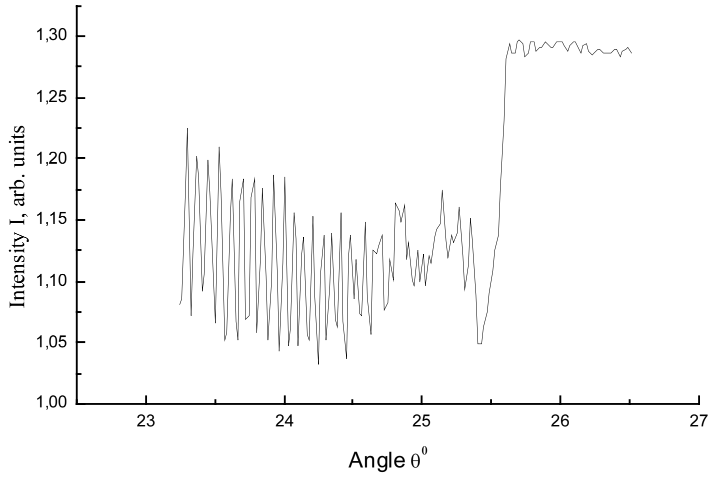

Fig.3. Light intensity as a function of the incidence angle for *p*-polarization for brine. n=1.333

2.3. The light interference in a flat cell.

The transmittance (λ=0.6328μm) of the cell as a function of the incidence angle was measured using a motorized computer controlled set-up. The cell was rotated with the step 0.01 degree. To distinguish the effects caused by the trivial Fabri-Perrot cavity, we have performed the same measurements for the empty cell and for the L_3 phase cell. The obtained results are shown in fig.4 and fig.5.

Two periods of modulation can be recognized in fig. 4,5. The fringes with small periodicity correspond to the thickness of the 1mm thick glass substrates. The larger period corresponds to the thickness of the gap between the substrates. The calculation gives the same value of the refractive index of the L_3 phase as it was obtained by TIR technique and was equal n=1.345. There is no qualitative difference in the transmittance of the L_3 phase cell in comparison with the empty cell for the *s*-polarization (Fig.4a,5a). The quantitative difference is a result of the difference in the refractive indices of the L_3 phase and air. Thus, the existence of the surface film is not evident from the transmittance for the *s*-polarization. It might indicate that the interface between the surface layer and the bulk L_3 phase is not sharp.

The anomalies (additional modulation) are present in the transmittance of the *p*-polarization for the L_3 phase with respect to the corresponding result for the empty one. It might be the result of the optical anisotropy of the interface. The calculations of the numerical value of the optical anisotropy require an exact model for the structure of the interface and are quite complicated.

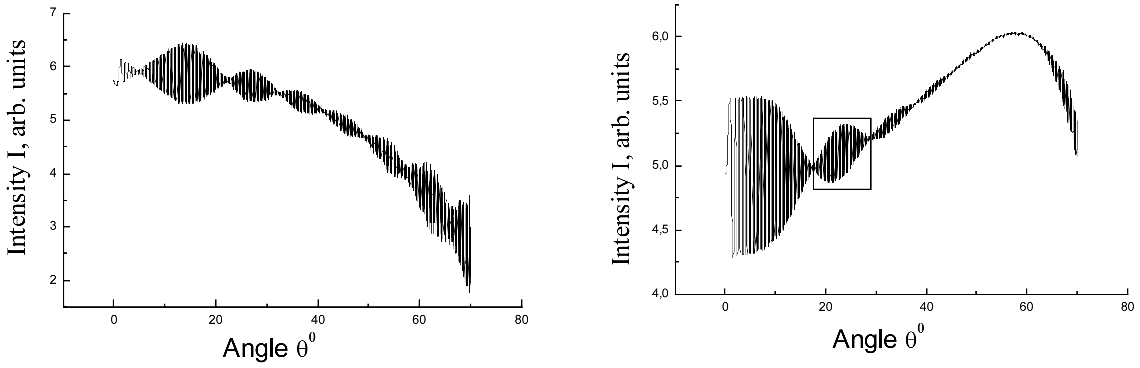

Fig.4. Interference fringes: a) *s*-; b) *p*-polarization for the empty cell.

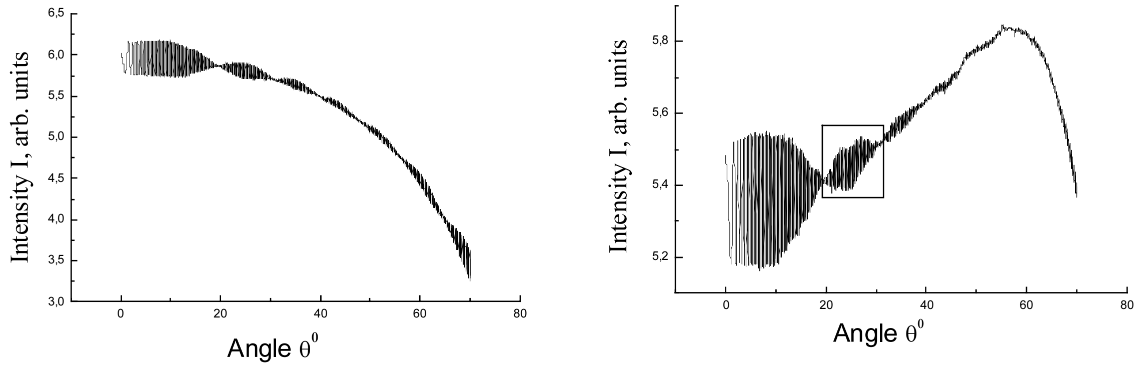

Fig.5. Interference fringes: a) *s*-; b) *p*-polarization for L_3 phase.

3. Conclusion

The solid substrate induces thin layer on the interface with L_3 phase. This layer has anisotropical properties, different from that of the L_3 phase. The structure of this layer can be defined as a set of parallel bilayers connected by passages, the number of which increases with increasing the distance from the surface. In such a way the structure of the surface layer smoothly transits into the bulk L_3 phase. In other words the surface layer is the L_α phase in which the order parameter vanishes smoothly with increasing the distance from the interface. The interlamellar distance in the surface layer is smaller than the corresponding value in the bulk.

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