

Lyotropic Chromonic Liquid Crystals: Effects of Additives and Optical Applications

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Abstract

We describe effects of ionic and neutral additives on phase and structural behavior of the lyotropic chromonic liquid crystals used in preparation of optical elements such as polarizers and compensators.

1. Introduction

Lyotropic Chromonic Liquid Crystals (LCLC) represent a distinct class of liquid crystals [1] with promising applications in various fields ranging from optical elements (polarizers [2-6] and compensators [7]) to biosensors [8]. LCLCs form in water solutions thanks to a one-dimensional aggregation of plank-like molecules with rigid aromatic cores and ionic groups at the periphery. In the so-called H-aggregation mode, the molecules are stacked face-to-face forming cylindrical aggregates; with an increasing volume fraction ϕ , a water solution of the material shows a progression from an isotropic (I) phase to nematic (N), columnar (C) and crystalline (Cr) phases, Fig.1. Evidently, phase and structural behavior of LCLCs should depend on ionic content of the solution. Ionic additives are expected to modify both the intra-columnar (between the molecules belonging to the same aggregate) and inter-columnar interactions, by altering electrostatic repulsive forces between the charged groups at the lateral surfaces of aggregates. When the additives occupy a substantial volume fraction of the solution, then other effects, such as depletion forces and “molecular crowding” might enter to the scene. In this work we demonstrate that there are three different scenarios of the additives’ effect on LCLCs:

(a) enhancement of the N phase upon addition of mono- and divalent salts of small size (so that the excluded-volume effects of the salts can be neglected);

(b) suppression of the N phase through its phase separation into coexisting I and C phases, upon addition of neutral species such as polyethylene glycol and uncharged spermine (Spm) in the free base form, caused by “molecular crowding” effects;

(c) condensation of the I phase into a liquid crystalline (N or C) phase upon addition of charged multivalent ions such as Spm(+4) salt, caused by the altered electrostatic forces.

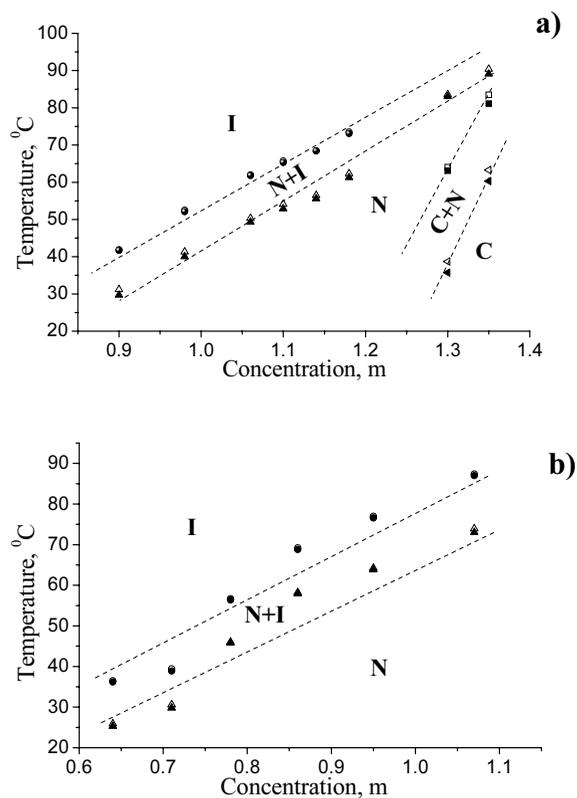


Fig. 1 Phase diagrams of Sunset Yellow (a) and Allura Red (b).

2. Phase diagrams and additives effect

Phase transitions in LCLCs such as Sunset Yellow (SSY) [9] and Allura Red are sensitive to both concentration and temperature, Fig.1. The latter feature is unusual from the point of view of the Onsager type theories. The reason is that the LCLCs are formed by aggregates of variable length that depend on the temperature, as evidenced by the experiments [10] and theory [11].

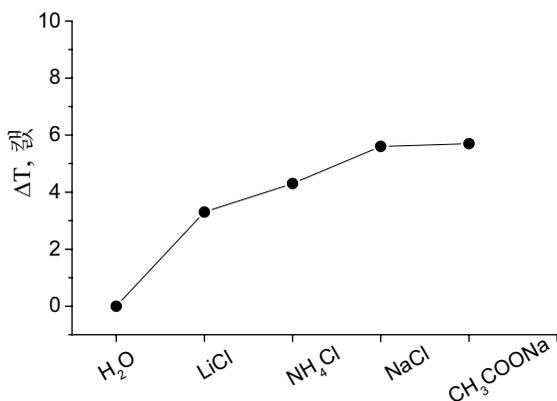


Fig. 2. Increase of the N-I transition temperature upon addition of 0.5 m of salts to 0.9 m SSY water solution.

Additives of mono and divalent salts of small concentration enhance the stability of N phase, raising the temperature of the N-I transition, Fig.2. The phenomenon can be understood in terms of the screening action of the salt that increases the so-called scission energy δ needed to divide one LCLC aggregate into two. In dilute solutions, one-dimensional aggregation of neutral species results in a broadly polydisperse distribution of aggregate lengths with the most probable length determined by ϕ , δ , and temperature T : $\bar{L} \propto \sqrt{\phi} \exp(\delta/2k_B T)$ [12]. For SSY, $\delta \approx 7k_B T$ [9]. The effect of salts can be estimated by assuming that electrostatic repulsion between charges of the adjacent molecules contributes to the value of δ (by decreasing it) and that ionic additives screen this repulsion and thus increase δ . In a very rough approximation, the change can be estimated as $\Delta\delta \sim -k_B T \times n \times l_B / r$, where $n=2$ is the number of charged groups per molecule, $l_B = e^2 / 4\pi\epsilon\epsilon_0 k_B T \approx 0.7 \text{ nm}$ is the Bjerrum length, ϵ is the dielectric permittivity of water, e is the elementary charge, and $r \leq 1 \text{ nm}$ is the typical

distance between the charges. Therefore, the electrostatic screening can increase δ by 10%-20% and thus significantly increases \bar{L} , enhancing the N phase (increasing the N-I transition temperature). In a less naïve approximation, the change in δ can be estimated as [13] $\Delta\delta \approx -dk_B T / 2l_B \sqrt{\phi + d^2 / 4\lambda_D^2}$, where the Debye screening length $\lambda_D = \sqrt{\epsilon\epsilon_0 k_B T / e^2 \sum_i c_{si} q_i^2}$ is determined by (molar) concentration c_{si} and valency q_i of the added salt species. For a typical $c_{si} = 0.3 \text{ M}$ and $q_i = 1$, one finds $\Delta\delta \sim - (0.1-1)k_B T$, i.e. significant. However, one should note that the validity of the model [13] is restricted by the relatively low concentrations, $\phi \leq 0.1$, thus these estimates should be viewed only as a qualitative support of a tendency of aggregates to elongate when the concentration of the salts screening the surface charges is increased.

Multivalent additives such as spermidine free base $\text{NH}_2(\text{CH}_2)_3\text{NH}(\text{CH}_2)_4\text{NH}_2$ (Spd), spermine free base $\text{NH}_2(\text{CH}_2)_3\text{NH}(\text{CH}_2)_4\text{NH}(\text{CH}_2)_3\text{NH}_2$ (Spm) and their salts Spd3HCl and Spm4HCl produce very different results depending on the degree to which they are charged, on their concentration c_s , and on ϕ .

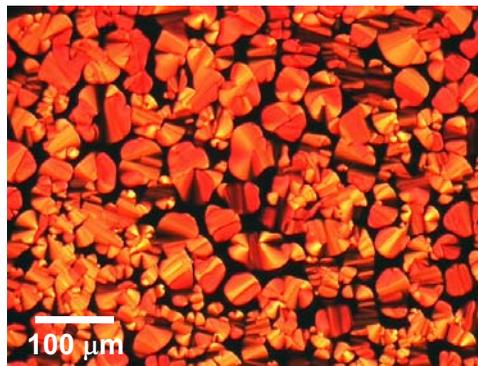


Fig. 3. Polarizing microscope texture of 0.5 m SSY with 0.1 m Spm(+4) salt; coexisting I and C phases.

(a) For low concentrations of SSY (0.5 m) that corresponds to I phase, addition of small quantities, $c_s = 0.1 \text{ m}$, of a salt Spm4HCl that exists predominantly as highly charged cations Spm(+4), leads to formation of the C phase inclusions in the I matrix, Fig.3. The same result is obtained when 0.3 m

of Spm(+4) salt is added to 0.7 m solution of SSY. The effect is similar to DNA condensation caused by charged multivalent ions such as Spm(+4), and Spd(+3) [14]. It can be explained by the attractive electrostatic forces between the columns triggered by multivalent ions. The multivalent ions screening the surface charges of the aggregates are well-separated along the aggregate axis. For Spm(+4), the typical distance between them can be estimated as $2d_z = 0.68 \text{ nm}$, where $d_z = 0.34 \text{ nm}$ is the molecular separation along the axis of the LCLC aggregate [9]. Surface-to-surface separation of the two SSY cylinders in the LC phase is smaller than that, according to the X-ray data [9], $\Delta \approx 0.3 \text{ nm}$. Therefore, the average size of the “+” and “-” charged patches at the cylindrical surfaces of aggregates is larger than the separation between the adjacent cylinders and the two system of patches can interlock into the geometry with “+” patch of one cylinder facing the “-” patch of the other cylinder, i.e., with an electrostatic attraction between them [15].

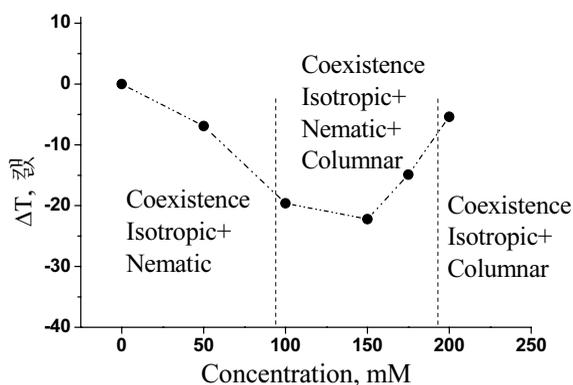


Fig. 4. Replacement of the N phase with a coexisting I+C phases upon addition of Spm free base for a solution of 34 wt% of SSY in water.

(b) For highly concentrated samples, with molal concentration of SSY higher than 0.9 m, which corresponds to the N phase, adding Spm or Spd in a free base form leads to a different result: The temperature range of the N phase shrinks and the phase is replaced with a coexisting I and C phases, Fig.4. The attractive forces leading to close packing of aggregates within the C phase should be associated with the depletion forces (“molecular crowding”) effects rather than with the electrostatic interactions.

The reason is that by adding the Spm free base in large quantities, one increases pH of the water solutions of SSY. We determined experimentally that pH grows from 6.5 to 11.3 when the concentration of Spm free base is increased from 0 to 0.2 M. At high pH, Spm molecules are mostly uncharged. Their conformation should be close to the statistical sphere of a diameter $\sim 1 \text{ nm}$ (the length of fully extended Spm molecule in the charged state is about 2 nm). Therefore, the SSY+Spm (free base) solution can be considered as a mixture of cylindrical rods and spheres of about the same diameter 1 nm. According to the numerical simulations [16], for sufficiently high concentration of the spheres, such a system is not stable and should demix into I phase with low SSY content and high Spm concentration and N phase with high SSY and low Spm content.

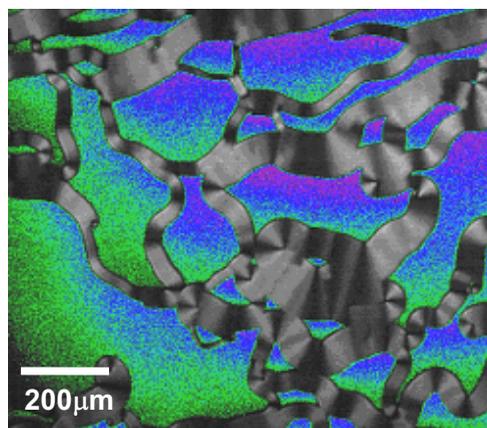


Fig. 5. Demixing in the system DSCG (grey birefringent parts of the texture) and PEG (fluorescent colorful parts).

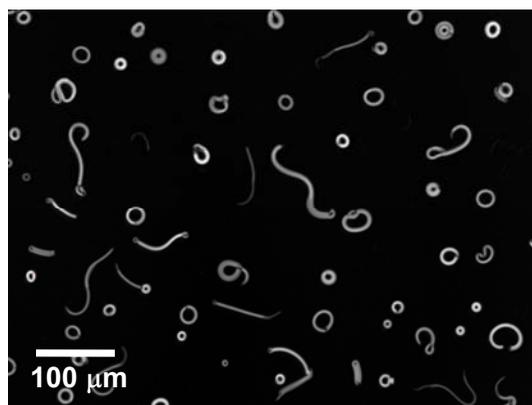


Fig.6. Formation of filaments and toroids of C phase in DSCG-Spm system upon cooling from the I phase.

To demonstrate the very possibility of demixing, we performed experiments with a mixture of LCLC disodium chromoglycate (DSCG) and polyethylene glycol (PEG) a portion of which has been labeled with fluorescent segments. We found that the PEG and LCLC completely demix, Fig.5. Demixing often leads to the formation of filaments and toroidal nuclei of the C phase that appears when the temperature is decreased and the system phase separates from the homogeneous I phase, Fig.6.

3. Effects of additives on dry films

One of the biggest problem in applications of LCLCs in the form of dry films is that they develop director undulations, often called “tiger stripes”. The distortions can be suppressed by additives [6]. Here we report the effect of additives on the dry films of commercially available LCLC material IR-806, that forms a LC for concentrations 0.7-10 wt% in water. The dried films of 1 wt% aqueous solution were used for investigation of the polarizing properties which are evident in the range (600-900) nm. Films were deposited from the solution in LCLC phase on glass substrates in unidirectional manner using a glass rod (or doctor blade) and dried at room conditions. The following materials were used as additives: polyvinyl pyrrolidone (PVP), polyethylene glycol (PEG), polyvinyl alcohol (PVA); block co-polymers: poly(dimethylsiloxane-b-ethylene oxide) (PDMS-b-PEO), poly(ethylene glycol-b-propylene) (PEG-b-PP)surfactant cetylpyridinium chloride (CPCI); glycerol. All materials were purchased from Sigma Aldrich Corp., except poly(dimethylsiloxane-b-ethylene oxide) block co-polymer purchased from Polysciences, Inc.

The dried films of IR-806 1 wt% show an anisotropic light transmission with a maximum for the polarization of light parallel to the shear direction. The films contain numerous tiger stripes that can be suppressed upon addition of a small amount (<1 wt%) of block co-polymer PDMS-PEO, Fig.7. Adding PVP ($M_w=10000$), PEG ($M_w=8000, 10000$), PVA ($M_w=13000-23000$), surfactant CPCI, glycerol do not eliminate undulation structure of the films. The main feature of PDMS-PEO is a low surface tension of hydrophobic PDMS chains. PDMS-PEO block copolymer with higher molecular weight ($M_w=5800$) produces better aligned films than the lower-molecular weight analog with $M_w=1200$.

4. Acknowledgements

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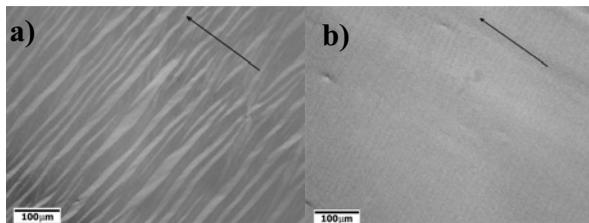


Fig. 7. Dry films of IR-806 without (a) and with (b) block copolymer PDMS-PEO. The arrow indicates the direction of shear/director alignment.

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