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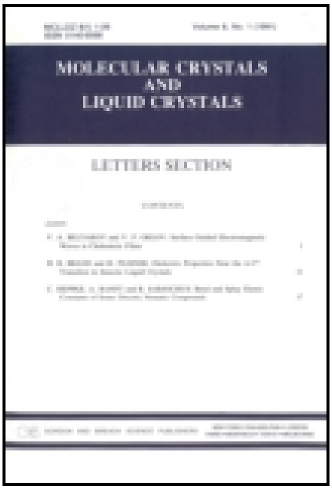

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Aggregation of Anthraquinone Dye Molecules in a Nematic Liquid Crystal

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We report an experimental evidence that molecules of anthraquinone dye aggregate in an anisotropic solvent, a nematic liquid crystal (NLC). We observe strong nonlinear dependencies of the dielectric permittivity and anisotropy of light absorption on the dye concentration c. Moreover, the data suggest that the aggregates are linear, but, in contrast to the isotropic case, their formation in a NLC undergoes two different concentration regimes with a well pronounced crossover. These effects are explained by the interplay between the aggregates' lengths and their orientational ordering due to the interaction with the nematic director.

Keywords Dye aggregation; nematic solvent; concentrational nonlinearity

1. Introduction

One of the most fundamental effect, which makes the state of solute molecules in solutions qualitatively different from their individual states, is a self-assembling of solute molecules into supramolecular aggregates [1]. Until recently, only isotropic solvents have been used in laboratories, and only aggregation effects in isotopic liquids have been considered theoretically [1, 2]. Over the last two decades, anisotropic hosts have also attracted researchers' attention [3–6], and there appeared reports on gel formation and aggregation in a dye-doped anisotropic solvent, a nematic liquid crystal (NLC) [7–11]. Moreover, the experimental data [9, 10] on a NLC doped with anthraquinone dye molecules gave rise to a hypothesis that the dye molecules formed rod-like aggregates whose interaction resulted in a strong macroscopic effect of reorientation of the nematic anisotropy axis (called the director [12]). Later, findings of Ref. [11] apparently pointed at a possible aggregation of dye solute in a cholesteric liquid crystal. The first theory of aggregation in an anisotropic solvent, a NLC, has been developed [13, 14].

In aqueous solutions many dye molecules are known to aggregate into supramolecular units of different shapes [15, 16]. The dye molecules are rigid, disc-like or plank-like, and

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tend to connect face-to-face and form linear stacked structures. The linear aggregates are columns whose lengths can reportedly be as large as several tens or even a few hundred molecules [17]. This anisotropy is so high that a dye concentration c of about 4% results in a liquid crystalline ordering of the aggregates (the so-called lyotropic chromonic liquid crystals [15, 16]). The liquid crystalline order is the result of the interaggregate interaction which can be well understood in terms of the Onsager approach [18]: the excluded co-volume and the free energy decrease as the orientational order of rodlike aggregates increases. The orientational order and aggregation numbers are coupled: reducing the excluded co-volume by increasing the orientational order parameter of the aggregate subsystem allows for a larger fraction of longer aggregates in the thermodynamic equilibrium [19]. We see that the orientational order in a lyotropic chromonic liquid crystals owes its existence solely to the interaction between aggregates, and thus requires sufficiently large concentrations, for otherwise aggregates are not long enough for substantial coupling. But in an anisotropic solvent such as a NLC, the orientational order of solvent molecules exists without any solute and, in principle, can manifest itself even for very small solute concentrartions provided that this nematic order is somehow coupled to the solute orientation. It is clear that particularly strong effects of this kind can be expected if the solute molecules form elongated suparamolecular structures.

In a NLC, prolate molecules are, on average, oriented along the director. The degree of their orientational distribution is described by the nematic scalar order parameter S. A new effect, which can be expected in such an anisotropic solvent, is a coupling between its anisotropy, described by S, and the distribution of numbers of molecules in aggregates (aggregation numbers) which determine the orientational solute-solvent coupling via the aggregates' anisotropy. In this paper we report experimental data showing the presence and orientational ordering of such structures in a solution of anthraquinone dye molecules in a NLC 5CB. These data provide evidence of an aggregation in anisotropic solvent and show that it is substantial even for small dye concentrations of the order of a fraction of a percent and that the solvent anisotropy brings about new effects absent in isotropic solutions.

Our approach to the search for the dye aggregation phenomena and, most importantly, to establishing the very fact of dye aggregation is in studying different properties of solutions as functions of a small solute concentration c. The main idea is that if the solute is present in the form of monomers, its contribution to macroscopic properties of the solution must be proportional to c; while otherwise it can be nonlinear. Indeed, any concentrational nonlinearity indicates an interaction between dye molecules. On the other hand, for a low $c < 0.01$, dye molecules in the pure monomer state would be separated by tens of solvent molecules and could not interact with one another. Therefore, any observed nonlinearities unambiguously imply that dye molecules interact with one another which, for such small concentrations, is possible only if, in the solution, they are present in the form of supramolecular aggregates.

A solution of anthraquinone dye molecules in a standard NLC 5CB was experimentally studied in Refs. [9, 10]. In 1990, an extremely strong light-induced effect of director reorientation was discovered in this system for very small dye concentrations c of the order of a fraction of a percent [3]. The data obtained in Refs. [9, 10] showed a variety of effects that are strongly nonlinear in c even for that low c; which resulted in a hypothesis of dye aggregation in a NLC. In this paper we further studied this system and found strong evidence of dye aggregation and a number of new effects related to it. These findings can be briefly summarized as follows. Dye molecules self-assemble into highly alongated aggregates whose formation and lengths are strongly enhanced for higher concentrations. The orientational order of aggregates can be described by their orientational order parameter

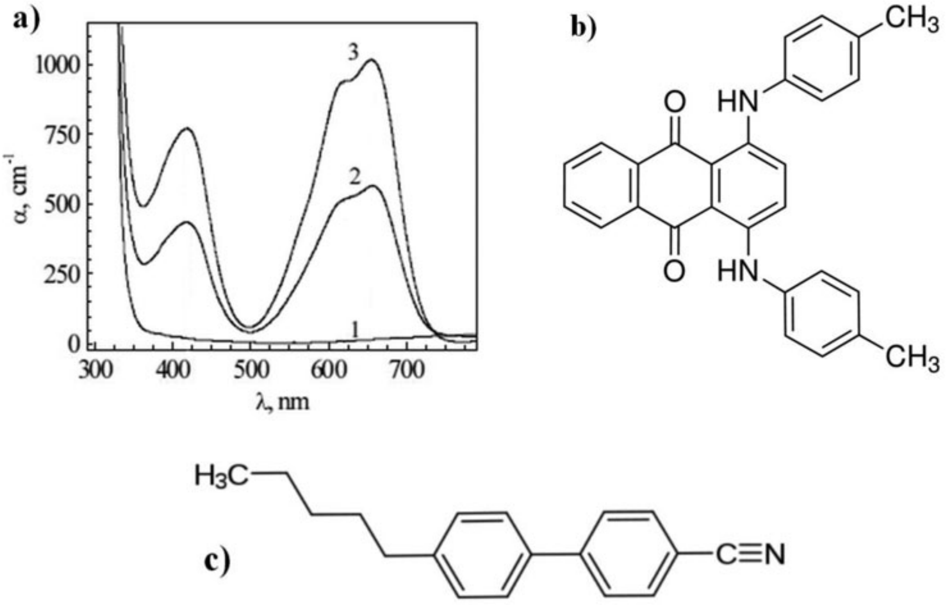

Figure 1. Optical absorbance of 5CB (**a, line 1**), anthraquinone dye (**a, line 2: –** $c = 0.006$**, line 3:** $c = 0.01$) and chemical structure of anthraquinone dye (**b**), 5CB liquid crystal (**c**).

S_a which increases with c and has apparent tendecy to saturate at the value $S_a \sim 0.3$ for high c. For $c \geq 0.01$, the aggregates segregate in their lengths and a dense phase, consisting of the longest aggregates, appears in the form of thin and very long dark strings ("whiskers") traversing the NLC (Fig. 3). The c dependencies of the cubic dielectric susceptibility and temperature T_{NI} of the NLC-isotropic liquid phase transition show, in contrast to the case of isotropic solvents, two different aggregation regimes with a pronounced crossover area around $c \sim 0.0026$: The existence of two distinguishable aggregation regimes is in line with the recent theory [13, 14] of aggregation in anisotropic solvents.

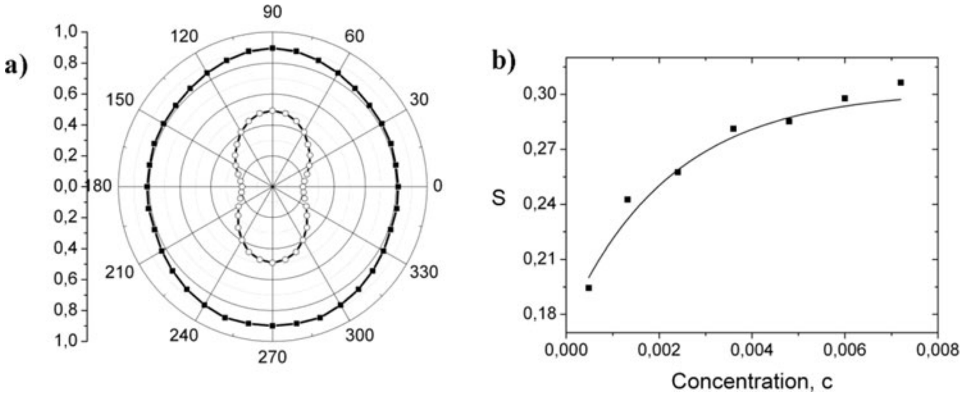

Figure 2. Optical anisotropy of light transmittance for $c = 0.0005$ (○) and $c = 0.006$ (■) of anthraquinone dye in 5CB (**a**) and order parameter for different dye concentration (**b**).

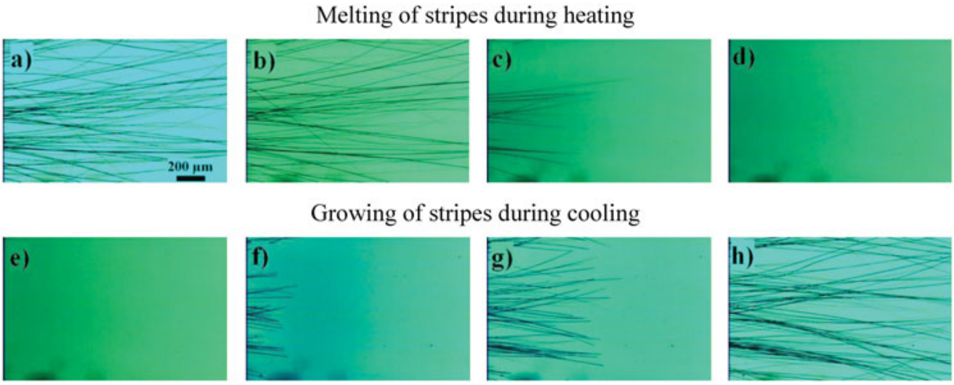

Figure 3. Melting (**a–d**) of anthraquinone "stripes" after heating and growing (**e–h**) after cooling. $T_{NI} = 33°C$, $c > 0.01$. Nematic phase T = 30°C (**a**); t = 20 min after nematic-isotropic transition, T = 50°C (**b**); t = 45 min after transition, T = 60°C (**c**); t = 1.5 hours after transition, T = 60°C (**d**). Isotropic phase, T = 40°C (**e**); t = 30 min after transition, T = 27°C (**f**); t = 3 hours after transition, T = 27°C (**g**); t = 2 days after transition (**h**). Images were captured by CCD Camera (Hitachi KP-D20BU) using polarizing microscope (Olympus BX51).

2. Experimental

We studied NLC pentylcyanobiphenyl (5CB, Merck) doped with an antraquinon dye N,N′-(methylphenil)-1,4 diamino-anthraquinon (D4) known to induce the optical response [3, 10]. The chemical structure and optical absorbance of the dye and 5CB are shown in Fig. 1. The dye was dissolved in the nematic material by gently heating to about 40°C. The solubility of this dye was good and concentration up to 1.7 wt.% was achieved. Further we will define dye concentration as following: c = (number density of dye molecules)/ρ_0, where $\rho_0 \approx 10^{27} \mathrm{m}^{-3}$ is the number density of the 5CB molecules ($c = 0.01$ corresponds to 1.78 wt.%). For each concentration used in experiment the separate solution was made. The solutions were allowed to mature for about 24 hours in the dark. Temperature and enthalpies of the phase transitions were determined using differential scanning calorimetry [20, 21] (DSC 404 F1 Pegasus® (NETZSCH)). Heating and cooling runs were carried out at the very slow scanning range, 0.1 K/min, ensuring thermodinamic equilibrium.

Bare flat glass plates, 2 mm thick, were used as substrates for cells. To reduce all organic and inorganic residues, glass plates were cleaned in an ultrasonic bath using distilled water and then rinsed in isopropanol and blown dry with air. The glass plates were spin coated with polyimide PI 2555 (Nissan Chemical) and treated for homogeneous alignment. Finally they were cured at 150°C for 20 minutes. The cells assembled with two identical polymer coated substrates, separated by two Mylar stripes (thickness is 15 μm), were filled with the 5CB solutions of anthraquinone dye. Filling of the cell was performed along the rubbing direction at temperature of about 10°C higher than the T_{NI} temperature.

The nematic scalar order parameter of aggregates is the coefficient of the second order Legendre polynomial in the polynomial of their orientational distribution function. It has the form $S_a = 1/2(3 < \cos^2\theta > -1)$, where θ is the angle made by the actual direction of the long axis of a given aggregate and the director, and $<\cos^2\theta>$ denotes the 3D thermodynamic average. For a light absorbing nematic, the value of $<\cos^2\theta>$ can be deduced from the dichroic ratio $N = k_{||}/k_{\perp} = \ln T_{||}/\ln T_{\perp}$, where $T_{||}$ and $T_{\perp}$ are the light transmittances measured for the light polarized, respectively, parallel and perpendicular to the director.

Finally, scalar order parameter obtains in the form $S_a = (N-1)/((N+2)(1-(3/2)\sin^2\beta))$, where β is the angle between the aggregate axis and dipole moment of the molecule [22].

Continuous laser generation TEM$_{00}$ single-mode CW He-Ne laser ($\lambda = 633$ nm, 75 mW) was used for dielectric susceptibility measurements by Z-scan technique [23].The focused laser beam with Gaussian profile was normal to the NLC cell thickness of $h = 10\ \mu m$ with the homeotropic director n$_0$ (E $\perp$ n$_0$). The intensity of light passing through the sample and a fixed diaphragm, vs the incident light intensity was measured [10].

3. Results and Discussion

3.1 Effects of Orientational Ordering vs Dye Concentration

3.1.1 Anisotropy of light transmittance. The optical anisotropy of the cells were measured with UV-Vis Srectrophotometer (SHIMADZU UV-2450) for a light wavelength $\lambda = 656$ nm at which the whole absorption is related to the dye molecules while absorption of the nematic host is negligible (Fig. 1a). For very small c (down to 0.0005) the optical anisotropy is only slightly detectable, but it becomes more and more pronounced as c increases. The order parameter S_a increases with c and has apparent tendecy to saturate at the value $S_a \sim 0.3$ for high c (Fig. 2b).

If dye molecules were in the form of the monomer, the sample transmittance would drop linearly with their concentration without changing its anisotropy. Therefore, the observed effect has to be attributed to certain orientational effect of the nematic molecules on the supramolecular units formed by dye molecules. A plausible geometry of such aggregates, which naturally explains the effect, is a rod-like stack of dye molecules with their planes nearly normal to the rod axis: for higher c the average rods are longer and the orientational effect upon them is stronger. This picture is strongly supported by the effect we observed for concentrations higher than 0.01, which is descibed below.

3.1.2 Aggregate length segregation and growth of dark strings. In samples with the dye concentration higher than 0.01, one observes a formation of long thin dark strings in a NLC (i.e., for temperatures $T < T_{NI}$), Fig. 3. This effect is thermodynamically reversible: i) increasing the temperature within the nematic range of the solution eventually results in thinning the strings whereas the temperature decrease results in their thickening; ii) strings that appeared in the nematic phase slowly disappear in the isotropic phase when the temperature is brought above T_{NI}; and slowly reappear when the temperature is again brought below T_{NI}; iii) reappering strings do not reproduce their previous shape and location; iv) the characteristic times of these effects are hours or even days; v) eventually the strings relax to the state that does not change with time and seems to be in thermodynamic equilibrium.

The size of strings and total volume of the dark matter strongly increase with the dye concentration and, in particular, the dark matter does not appear for c below some threshold, $c \sim 0.01$. Below this concentration we did not observe any visible changes in the LC structure. As the aggregation of dye is mainly a one dimentional crystallization. The highly elongated string structures indicate that the aggregation is mainly a one-dimensional process. The strings, whose directions do not necessary coinside with LC director, have diameters in the range of a couple of hundreds of nanometers (Fig 3). Meanwhile their length may reach hundreds of micrometers. Similar string-like structures were observed in a solution of dye AG1 in a NLC E7 [24] which supports the idea of one-dimensional aggregates in NLCs. One-dimensional structures were also observed for cyanine dyes in

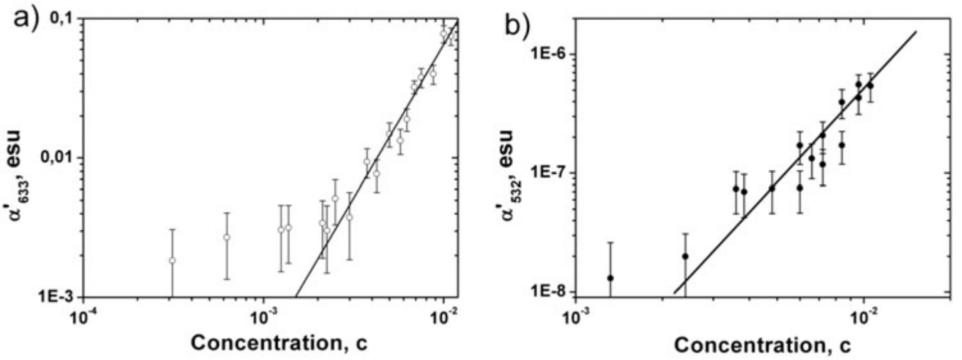

Figure 4. Coefficient $\alpha'_{633}(c)$ for laser wavelength $\lambda = 633$nm (**a**); solid line: $\alpha'_{633} \sim c^{2.75}$ and $\alpha'_{532}(c)$ for $\lambda = 532$nm (**b**); solid line: $\alpha'_{532} \sim c^2$. Homeotropic 10 μm cell [9, 10].

polar isotropic solvent [25–27]. The above results indicate that crystallization of the D4 in the 5CB liquid crystal starts from the formation of one dimensional molecular aggregate far prior the crystallization becomes visible. Unlike isotropic liquids where the length of aggregates are solely described by the configurational free energy, related to the elastic energy and conformational entropy of flexible linear aggregates, the orientational interaction of aggregates with the anisotropy of a NLC enhances the aggregate length, giving rise to areas rich of longest aggregates which take the form of strings [28].

3.2 Cubic Dielectric Susceptibility and Temperature of the NLC-isotropic Liquid Transition of the Solutions

Interaction between the dye molecules is evidenced by a strongly nonlinear dependence of the polarizability $\alpha = \alpha_L + \alpha' E^2$ on the dye concentration c, where α_{L} and α' are independent of the field amplitude E (for the reason clarified in [10], the standartd notation $\chi^{(3)}$ for α' is not used). If dye molecules do not interact, their contributions are additive and $\alpha \sim c$. For our system, we find $\alpha'(c)$ to be highly nonlinear. First, we measured α' for 5CB + D4 with continuous laser generation (TEM$_{00}$ single-mode CW He-Ne laser, $\lambda =$ 633 nm, 75 mW). The focused laser beam with Gaussian profile was incident normal to the NLC cell of thickness $h = 10$ μm with the homeotropic director alignment. We measured the intensity of light passing through the sample and a fixed diaphragm, as a function of the light intensity I. The dependence $\alpha'_{633}(c)$ is strongly nonlinear and shows two different regimes with the crossover around $c_c \sim 0.0026$: for small c, α'_{633} scales close to c^1 whereas for $c \geq c_c$; it changes to the power law close to $c^{2.75}$; Fig. 4(a).

To exclude the contribution from the NLC, the same cells were irradiated with picosecond pulses at $\lambda = 532$ nm: the absorption of 5CB at 532 nm is low and the optical response to picosecond pulses is weak [29]. A strongly nonlinear dependence $\alpha'_{532}(c)$; close to c^2, was observed in this case as well, Fig. 4b. The nonlinearity of $\alpha'(c)$ indicates a domination of supramolecular units in the optical response.

Another nonlinearity was observed in the c dependence of T_{NI} transition, Fig. 5a. Samples of calorimetric curves are shown in Fig. 5b. The measured heat capacity demonstrates no significant influence of dye concentration on the NI transition for small c, $c \leq 0.006$. However, a substantial broadening of the transition and shift of its temperature were observed for the concentration of about $c = 0.01$. The observations show a decrease

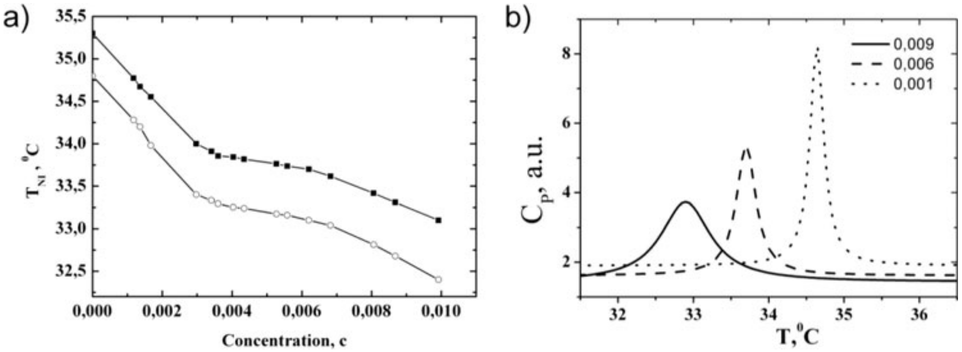

Figure 5. The nematic-to-isotropic transition temperature (**a**) and temperature dependence of heat capacity (b) for different anthraquinone dye concentration in 5CB.

of heat capacity with increase of concentration of non-mesogenic molecules. Both theory [30, 31] and experiment [4, 6] show that the variation of T_{NI} with the solute concentration is negative and linear. Our experimental data are still consistent with the model that predicts a decrease of the T_{NI} with increase of concentration of non-mesogenic molecules. There is, however, a clear difference in the slope of the linear dependence for small ($c \leq 0.0026$) and for larger ($c \gtrsim 0.0026$) dye concentrations.

The temperature T_{NI} is a monotonically decreasing function of dye concentration. However, it has a plato-like region of concentrations which begins at about $c_1 \sim 0.0026$ and ends at about $c_2 \sim 0.006$–0.008: In this region the dependence T_{NI} (c) is substantially weaker that that to the left and to the right thereof. The drop of T_{NI} (c) is primarily determined by the entropy increase due to impurities which, for small concentrations, is proportional to their concentrations. Therefore, had if the dye molecules been in the same state independent of c, $T_{NI}(c)$ would have been a linear function of c [4, 6, 31]. Thus, dependence $T_{NI}(c)$ shows that the dye molecules form supramolecular units and their total number is a nontrivial function of the concentration c. Moreover, it is probably not without a deep reason that the left end c1 of the plato region in the dependence $T_{NI}(c)$ is very close to the crossover concentration c_c found in the above dependence $\alpha'_{633}(c)$. The theory [13, 14] shows that self-assembling of solute molecules into quasi-one-dimensional worm-like aggregates in an anisotropic solvent can have two distinguishably different regimes for smaller and higher solute concentrations. We believe that both points, c_1 and c_c, correspond to the crossover from a low concentration regime to a large concentration regime of aggregation: at low c, the number of aggregates is increasing quickly with c, then at c_c the average aggregate length is fastly growing while the number of aggregates is increasing very slowly, which manifests itself in a plato in the curve $T_{NI}(c)$. The right end $c_2 \sim 0.008$ of the plato can be related to the onset of the interaggregate interaction which, at $c \sim 0.01$, results in the formation of the dark strings reach with the longest aggregates.

4. Conclusions

We present the experimental data which provide an evidence that anthraquinone dye molecules form aggregates in an anisotrpic solvent, a NLC 5CB. The aggregation in anisotropic solvents gives rise to new effects that are not pertinent to the dye aggregation in istropic liquids. First, the orientational effect in isotropic solutions occurs at sufficiently large c because of the interaggregate interaction which is weak for lower c. In contrast, an orientational effects in a NLC occur for very low concentrations due to the interaction of the nematic order with alongated aggregates which do not interact with one another. Second, our experiments show that, in contrast to the single dye aggregation regime in isotropic solvents, in NLCs there are two different aggregation regimes for lower and higher concentrations. Third, the aggregation in a NLC is so strong that for concentrations just slightly above 0.01, at which the aggregates would be too short and could not interact in isotropic solvents, the interaggregate interaction gives rise to the formation of long-aggregates-rich areas which appear in the form of long and thin strings proliferating through the whole bulk of the solution. These findings show, that the aggregation in anisotropic solvents presents interesting new perspectives in the physics of self-assembling, orientational interaction and related phase formation and coexistence. As a concluding remark we would like to emphasize that the idea of concentrational nonlinearity, which our approach is based upon, proves to be a general and poweful tool in the study of self-assembling phenomena.

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