Transparent Lyotropic Ferronematics

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Abstract

Transparent lyotropic ferronematic dispersions are synthesized by admixing a cationic ferrofluid to the lyotropic liquid crystal PL/1D/Wt. The transparency is spontaneous and time-independent. It is observed in zero magnetic field in white and polarized light for disordered layers of ferrofluid crystals of thicknesses $\geq 1 \text{ cm}$ in both isotropic and nematic phases. Justification of the low extinction of light in the systems of the lyotropic origin is presented.
Introduction

The goal of this letter is to discuss the nature of the transparency effect in lyotropic ferronematics. In general, the term ferronematic refers to a magnetically-sensitive complex fluid resulting from mixing together magnetic and liquid-crystalline components [1]. At present, three kinds of those media can be distinguished. Namely, ferronematics can be synthesized by admixing of (i) a paramagnetic ion dopant to a thermotropic liquid crystal [2], (ii) a ferrocolloid to a thermotropic liquid crystal [3], and (iii) a ferrocolloid to a lyotropic liquid crystal [4]. A ferrocolloid (often called ferrofluid) is a colloidal dispersion of superparamagnetic nanoparticles in a liquid carrier. The problem of primary importance for ferro-liquid-crystalline compositions is their ability to resist the spontaneous aggregation of the components. Recently, when solving the problem of colloidal stability for lyotropic ferrodispersions with high concentration of magnetic particles, we observed stable ferronematics, which were completely transparent in a white and polarized light [4, 5, 6].

The phenomenon of the liquid crystal transparency in thick samples (∼1 cm) is an issue of considerable interest [7]. It is well known [8] that high turbidity of thermotropic liquid crystals is due to the director fluctuations so that non-oriented thermotropics completely depolarize and disperse light even in thin (∼0.1 mm) layers. With lyotropics we observed liquid crystals, which, being in the non-oriented state, completely depolarize light but are transparent. It is well known that occurrence of a similar effect in colloid systems means a low level of aggregation, i.e., the stability of the system. This property of ferrolyotropic dispersions helps a lot when investigating their phase diagrams [3, 4].

A ferrolyotropic dispersion inherits transparency from both its components: a ferrofluid and a pure lyotropic solution PL/1D/Wt, immaterial in which of the two states—nematic or isotropic—the latter is. This transparency is preserved in a broad temperature and concentration ranges and is long living. In below we present a qualitative discussion of the phenomenon by comparing light scattering intensities of classical thermotropics with those for lyotropic liquid crystals and colloidal magnetic dispersions.
Experimental

We use a lyotropic liquid crystal PL/1D/Wt, which is a ternary solution of potassium laurate (PL), 1-decanol (1D) and water (Wt). The said solution makes a lyotropic base for preparation of ferronematics. Potassium laurate is synthesized in the laboratory by alkalinization of lauric acid with potassium hydroxide. The details of synthesis are described in Ref. [6]. At 20°C the concentration ranges are normally 5–8.8 wt% for 1D and 62–68 wt% for water with the saturation pH value $\sim 10$. The obtained samples are completely transparent and uniform in both isotropic and nematic phases. The liquid crystal orients spontaneously, which process takes minutes in a thin ($\sim 0.1$ mm) glass capillary and a week in a thick ($\sim 10$ mm) glass tube. In non-oriented layers, these lyotropic solutions remain entirely transparent but depolarize the light completely [6], see the Fig. (a,b).

For the studied PL/1D/Wt compositions, the clearing points are not observed, neither with respect to temperature nor to concentration. In the nematic region at 20°C, a positive uniaxial optical anisotropy is detected. Positive birefringence implies that the mesophase is organized as a discotic structure. The micelle concentration in the lyotropic solution is about $10^{19}$ cm$^{-3}$. For similar systems in the same temperature range, the micelle diameter and thickness were found earlier by means of small-angle neutron scattering to be $\sim 6.4$ nm and $\sim 2.3$ nm, respectively [9].

Cationic ferrofluids are synthesized by the method described in Ref. [10]. They are stable aqueous colloids of $\gamma$-Fe$_2$O$_3$ under standard conditions: $pH \sim 2$ and temperature 20°C. Saturation magnetization of the dispersed maghemite particles is about $\sim 300$ G [11]. Their distribution is fairly well described by a log-normal function with the characteristic diameter 7–8 nm and the dispersion $\sim 0.3 – 0.4$. Concentration of the magnetic phase in the parent ferrofluid was about $\sim 5$ vol.%. The ferrofluids were optically isotropic under zero external magnetic field.

Lyotropic ferrodispersions are prepared with the method described in Ref. [5] that yields transparent and stable ferroliquid crystals, see Fig. (c,d). The content of the
magnetic component was $10^{-4} - 1$ vol.%. Characteristic red-brown color due to the presence of ferroparticles was observed for all the samples. Strong magneto-orientational effects at 10–100 Oe were detected for ferronematic layers of the thickness 0.1-10 mm, see Refs. [4, 12].

Light Scattering by Liquid-Crystalline Materials

Let us begin with the case a thermotropic nematic liquid crystal. In the isotropic phase, the main part is played by the density fluctuations in the liquid. In the ordered phase, the principal contribution goes from the director fluctuations. After Ref. [8], the ratio of scattering cross-sections in the nematic and isotropic states is

$$\frac{\sigma_n(t)}{\sigma_i(t)} \simeq \left[ \frac{\varepsilon_a(t)}{\varepsilon'(t)} \right]^2 \left[ K(t) q^2 \kappa(t) \right]^{-1}; \quad (1)$$

Here $q \sim 2\pi/\lambda$, where $\lambda$ is the wavelength. In Eq. (1) the dielectric anisotropy $\varepsilon_a(t)$ and the reference elastic constant $K(t)$ (Frank modulus) are the parameters inherent to the ordered state while the isothermal compressibility $\kappa(t)$ and the parameter $\varepsilon'(t)$ characterize the isotropic state. Note that hereafter we mark the material parameters referring to thermotropic/lyotropic substances by superscripts “(t)” or “(ℓ)”. For the order of magnitude estimate one can take $\varepsilon_a(t) \sim \varepsilon'(t)$.

With the same accuracy, one may set $\kappa \sim a^3/U$, where $U$ is the typical energy of the molecule coupling and $a$ is the reference molecular length, i.e., the size of the nematogenic chemical unit. For the elastic constant, in the same way one gets $K \sim U/a$. Given that, Eq. (1) reduces to

$$\frac{\sigma_n(t)}{\sigma_i(t)} \simeq 1/(qa)^2. \quad (2)$$

For small scattering angles: $q < 10^{-2}$ nm$^{-1}$.

In thermotropics, the structural unit is a single molecule with $a \sim 2$–3 nm. In result, from Eq. (2) one finds that the ratio (2) is about $10^6$. This estimation, first given in Ref. [8], shows that the nematic phase of a thermotropic mesogenic substance is six orders
of magnitude more opaque than its isotropic phase. This explains why thermotropic mesogens, on entering the ordered state, become completely turbid.

In a lyotropic solution, the elementary scattering unit is a micelle that floats in an isotropic liquid carrier. This entails a considerable difference between the light scattering mechanisms in lyotropic and thermotropic nematogens. Each micelle is an aggregate comprising a number of tensioactive molecules. In the considered here case of PL/1D/Wt, the micelles are anisometric with the maximum size \( a \) about \( \sim 5 \) nm. However, despite being a multi-molecular object, a micelle still remains an entity, whose size is much smaller than the optical wavelength. This enables one to treat a lyotropic nematogen as a continuous medium.

Assuming, as in the case of thermotropics, that in the ordered phase the main scattering is due to the director fluctuations, we retain in the cross-section ratio \( \sigma_{nem}^{(t)} \) only the term with the dielectric permeability anisotropy. Meanwhile, in the isotropic phase a lyotropic solution by its scattering abilities cannot differ much from the isotropic phase of thermotropic nematogens. Indeed, this scattering is caused by the long-wave density modulations, i.e., is determined by the volume elasticity (compressibility) of the liquid.

Thence, constructing in the same way as in Eq. (1) the cross-section ratio for a lyotropic case, one gets

\[
\frac{\sigma_{nem}^{(t)}}{\sigma_{iso}^{(t)}} \sim \frac{[\varepsilon_a^{(t)}/\varepsilon_a^{(t)}]^2 \left[ K^{(t)} q^2 K^{(t)} \right]^{-1}}{\phi^{-1}}, \tag{3}
\]

The most important difference between thermotropic and lyotropic systems is that, experimentally, all the known lyotropics are low-birefringent: their dielectric anisotropy \( \varepsilon_a^{(t)} \) is about \( 10^{-3} \) of their isotropic dielectric constant.

Relating the reference values of the scattering ratios for thermotropics and lyotropics under assumption that \( \varepsilon_a^{(t)} \sim \varepsilon_a^{(t)} \), one gets

\[
\frac{\sigma_{nem}^{(t)}}{\sigma_{nem}^{(t)}} \sim \frac{[\varepsilon_a^{(t)}/\varepsilon_a^{(t)}]^2 \left[ K^{(t)} / K^{(t)} \right]}{\phi^{-1}}, \tag{4}
\]

where the factor \( \phi \) that is the volume fraction of micelles in the solution. It has appeared due to the fact that in the ordered state only the scattering from micelles is taken into account.
account; we remark that in the PL/1D/Wt systems under study we have $\phi \sim 0.1$. The ratio $\varepsilon_a^{(t)}/\varepsilon_a^{(\ell)}$ may be expressed in terms of the refraction indices. We set $\varepsilon_a^{(\alpha)} = [n_{\varepsilon}^{(\alpha)}]^2 - [n_o^{(\alpha)}]^2 \sim n_o^{(\alpha)} \Delta n^{(\alpha)}$, where index $\alpha$ marks either of the nematics. For thermotropics one has $\Delta n^{(t)} \sim 10^{-1}$ and $K^{(t)} \sim 10^{-7}$ dyn whilst for lyotropics: $\Delta n^{(\ell)} \sim 10^{-3}$ and $K^{(\ell)} \sim 10^{-6}$ dyn; the values of $n_o$ for both substances are of the same order. This casts the ratio (4) in the form $\sigma_{nem}^{(t)}/\sigma_{nem}^{(\ell)} \sim 10^5/\phi$. As is shown in above, for a thermotropic nematogenic substance the scattering ratio is $\sim 10^6$ by itself, therefore for a lyotropic system the corresponding ratio, see Eq. (3), is $\sim 10\phi \sim 1$.

Thus we conclude that in the isotropic state thermotropic and lyotropic nematogens are equally transparent. On entering the nematic phase, a thermotropic nematogen becomes $10^6$ times more opaque whereas the transparency of a lyotropic liquid crystal is almost unaffected by the orientational phase transition. This falls in full agreement with the experimentally evidenced fact that even at a considerable sample thickness (tubes $\sim 1$ cm), lyotropic liquid crystals are completely transparent both in isotropic and nematic states.

In the case of a lyotropic ferronematic, the contribution to the light scattering that owes to the presence of magnetic grains should be taken into account. The main governing parameters are: the mean particle size $d$, particle number concentration $c$ and aggregation number $m$. The first two may be measured directly, and for our systems they are $d \sim 8$ nm and $C \sim 10^{14} - 10^{15}$ cm$^{-3}$.

To estimate the aggregation number, it is necessary to select the appropriate scenario of aggregation in the lyotropic ferronematic. In the studied case, the magnetic dispersions are rather dilute: the volume fraction of particles does not exceed 0.01 vol.% and so is far from any of the phase separation thresholds, see the diagrams in Refs. [5, 6]. Under such conditions, the main cause of aggregation is the interparticle magnetic dipole-dipole interaction [13], the intensity of which is measured by the value of the dimensionless parameter $\Lambda = \mu^2/k_B T d^3$ with $\mu$ being the particle magnetic moment and $T$ the temperature [14]. For single-domain particles one has $\mu = (\pi/6) M_s d^3$, where $M_s \sim 300$ G is the magnetization of the colloidal maghemite; at room temperature $k_B T \sim 4 \cdot 10^{-14}$ erg.
According to Ref. [15], depending on the value of \( \Lambda \), there are three qualitatively different modes of aggregation. At \( \Lambda < 1 \), the particles are well separated and do not aggregate. In the range around \( \Lambda \sim 3 \) a considerable number of quasi-spherical droplets comprising several particles is present. At \( \Lambda > 10 \), the particles form multi-grain open loops and long chain structures. With the above-mentioned mean particle diameter, for our systems estimation gives \( \Lambda \sim 3 \) that implies that the particles, in majority, are associated in quasi-spherical droplets with the aggregation number \( m \sim 4-6 \). Recalculating this into an effective aggregate diameter, one finds \( d^{(f)} \sim 16 \text{nm} \).

Let us compare the Rayleigh scattering parameter of a ferrofluid, \( R^{(f)} \), and that of a lyotropic colloid, \( R^{(\ell)} \). The pertinent formula, see Ref. [16] for details, simplified for the case of dilute colloids reads

\[
R^{(f)}/R^{(\ell)} \simeq \left[ C^{(f)}/C^{(\ell)} \right] \left[ d^{(f)}/d^{(\ell)} \right]^6 (\delta n)^{-2},
\]

where \( \delta n \) is the difference between the refraction indexes of the micelle and the solvent, \( C^{(f)} \) and \( C^{(\ell)} \) are the number concentrations of the scattering units. To estimate the ratio (5), we take for the concentrations \( C^{(f)} \sim 10^{14} \text{cm}^{-3} \) and \( C^{(\ell)} \sim 10^{19} \text{cm}^{-3} \), for the mean diameters \( d^{(f)} \sim 16 \text{nm} \) (a magnetic particle aggregate) and \( d^{(\ell)} \sim 3 \text{nm} \) (a micelle), and \( \delta n \sim 0.1 \) for the refraction indices difference. Hence, for the ratio (5) one finds \( R^{(f)}/R^{(\ell)} \sim 1 \). This estimate agrees well with the evidence presented in Fig. and proves explicitly that an admixture of magnetic nanoparticles up to \( \Phi \sim 0.07 \text{ vol.\%} \) does not cause any significant changes in the transparency of a lyotropic ferronematic in comparison with that of a “clean” lyotropic system.

### Conclusion

Synthesis of lyotropic nematic ferroliquid crystals, which are highly transparent, is reported that is done by admixing a cationic maghemite ferrofluid to the lyotropic solution PL/1D/Wt. According to qualitative considerations, the transparency is ensured by two principal circumstances. The first is quite universal and refers to the fact that light scat-
tering is proportional to the square of the optical anisotropy $\Delta n$. Since $\Delta n$ is low in all
lyotropic systems, accordingly, small is the corresponding contribution to the scattering.
The second factor is synthesis-sensitive. If a ferrolyotropic dispersion is stable enough, as
it happens for our samples, the mean aggregation number of magnetic nanoparticles does
not exceed several units. Because of that, the light scattering caused by the dispersed
solid phase remains less or at the same level as that of the micellar solution. Summariz-
ing, one can characterize the reported lyotropic ferronematics as anisotropic fluids, which
uniquely combine the low magnetic-field control over the optical axis direction and the
high optical transparency.
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Figure Caption

Fig. 1. Specimens of lyotropic solutions: (a) pure lyotropic in a white light, (b) pure lyotropic in a polarized light, (c) ferronematic in a white light; a concentration of the magnetic phase $\Phi = 0.04$ vol.$\%$, (d) ferronematic in a polarized light; the tube diameter is about 1 cm.

Figures

see the file.jpg in attach.
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