Liquid crystals doped with magnetic nanoparticles

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ABSTRACT

The paper presents an overview of the observations of structural transitions in ferronematics based on thermotropic nematics 4-cyano-4'octylbiphenyl (8CB) and 4-trans-4'-n-hexyl-cyclohexyl-isothiocyanato-benzene (6CHBT). The determination of the surface density of anchoring energy of nematic molecules on magnetic particles surfaces by the observations of the structural transitions in external fields is demonstrated on the example of the 8CB-based ferronematic. The ferronematic droplets were observed in solutions of nematogenic 6CHBT dissolved in phenyl isothiocyanate and doped with fine magnetic particles. The phase diagram of the transitions from the isotropic phase to the nematic phase via droplets was found. The magneto-dielectric measurements of various structural transitions in this new system enabled to estimate the type of anchoring of nematic molecules on magnetic particles surfaces in droplets.

Keywords: liquid crystals, magnetic nanoparticles, ferronematics

1 INTRODUCTION

The orientational order of liquid crystal can be easily controlled by rather weak electric fields due to the anisotropy of dielectric permittivity. However, because of the small value of the anisotropy of diamagnetic susceptibility ($\chi_a \sim 10^{-7}$), magnetic fields used for the same purpose have to reach rather large values ($B\sim$1T). In effort to enhance the magnetic susceptibility of liquid crystals, the idea of doping them with fine magnetic particles was theoretically introduced by Brochard and de Gennes. They constructed a continuum theory of magnetic suspensions in nematic liquid crystals (ferronematics) in their fundamental paper [1], prior to the chemical synthesis of these systems. In first experimental paper, Rault et al. [2] reported the basic magnetic properties of a suspension of rod-like γ-Fe_2O_3 particles in 4'–methoxybenzylidene–4–n-butylaniline (MBBA) liquid crystal. Later, based on the estimations given in [1], first lyotropic [3] and then thermotropic [4] ferronematics were prepared and studied.

One of the most important questions solved in the theory of ferronematics is the problem of the equilibrium orientation of magnetic particle, i.e. its magnetic moment $\boldsymbol{m}$, in the nematic matrix. The Brochard and de Gennes theory [1] considers the rigid anchoring with $\boldsymbol{m} \parallel \boldsymbol{n}$, where the unit vector $\boldsymbol{n}$ (director) denotes the preferential direction of the nematic molecules. Later, Burylov and Raikher [5] showed that Brochard-de Gennes theory is incompatible with real structure in some thermotropic ferronematics and they proposed modification. They consider the finite value of the surface density of anchoring energy W at the magnetic particle - nematic boundary. The finite value of W, as well as the parameter $\omega=Wd/K\leq 1$, characterize the soft anchoring of nematic molecules on magnetic particles surfaces (d - typical size of magnetic particle, K – corresponding Frank orientation-elastic modulus of liquid crystal). The soft anchoring, unlike the rigid, permits both types of boundary conditions ($\boldsymbol{m} \parallel \boldsymbol{n}$ and $\boldsymbol{m} \perp \boldsymbol{n}$), thus the Burylov and Raikher's theory could be applied for thermotropic ferronematics. In its frame the instabilities of the uniform texture in ferronematics exposed to external magnetic or electric field (Freedericksz transitions) [6,7] were studied and the expressions for their critical fields in different geometries were found.

This paper presents an overview of the results obtained in the study of structural transitions in ferronematics based on different thermotropic nematics (8CB and 6CHBT) and in ferronematic droplets. The experiments with ferronematic droplets were inspired by the work of Kedziora et al [8], who observed a droplets of nematic liquid crystal dissolved in non-polar medium in the vicinity of isotropic-nematic transition. We have studied magnetically active ferronematic droplets in isotropic phase, i.e. nematic droplets containing magnetic nanoparticles. The aim of our work was to find the phase diagram of prepared mixture of nematic liquid crystal dissolved in non-polar medium with magnetic particles and to determine the type of anchoring of nematic molecules on magnetic particles surfaces in studied ferronematic systems.

2 EXPERIMENT

Studied ferronematic samples were based on two types of thermotropic nematics: 4-cyano-4'octylbiphenyl (8CB) and 4-trans-4'-n-hexyl-cyclohexyl-isothiocyanato-benzene

(6CHBT). The temperature of the nematic-to-isotropic transition of studied nematics is t_{N-I} = 40.5ºC for 8CB and t_{N-I} = 42.8ºC for 6CHBT. The nematic samples were doped with magnetic suspension consisting of Fe_3O_4 particles coated with oleic acid as a surfactant (mean diameter D_v=10nm, standard deviation σ=0.28). The doping was simply done by adding this suspension, under continuous stirring, to the liquid crystal. The small volume concentrations of magnetic particles (~10^{-5} to ~10^{-3}) and surfactant in prepared ferronematic samples avoid the interparticle dipole-dipole interactions. The homogeneity and stability of the samples were verified by optical microscopy and by dielectric measurements. The dielectric properties of very diluted magnetic colloids depend on the volume concentration and dispersion of magnetic particles. The parameter of anisotropy is defined as

$$g(H) = -\frac{\varepsilon_{II}(H) - \varepsilon_0}{\varepsilon_\perp(H) - \varepsilon_0}, \qquad (1)$$

where $\varepsilon_{||}$ and $\varepsilon_\perp$ are dielectric permittivity measured for electric field parallel and perpendicular to the applied magnetic field, respectively, ε_0 is dielectric permittivity without field. In well diluted dispersed magnetic colloids parameter of anisotropy reaches the constant value $g(H)$=2 [9]. The presence of aggregates violates this equality [10]. Our measurements (performed with the accuracy up to aF) showed, that the value of $g(H)$ is close to 2, as it is illustrated in Fig.1 for the 8CB-based ferronematic with volume concentration of magnetic particles Φ =5.10^{-4}. The $\varepsilon_{||}$ and $\varepsilon_\perp$ were obtained from capacitance measurements. This is a proof of the absence of aggregation in studied samples. The $g(H)$ dependences of 6CHBT-based ferronematic was very similar to that presented in Fig.1.

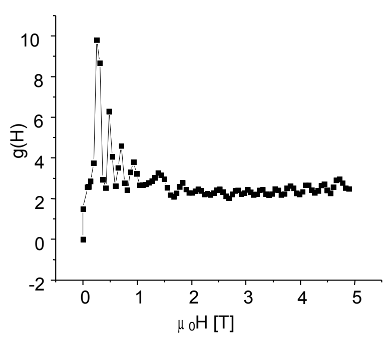

Figure 1: The $g(H)$ dependence measured in 8CB-based ferronematic with volume concentration of magnetic particles Φ=5.10^{-4}.

The formation of the ferronematic droplets was achieved near the isotropic-nematic transition temperature, in the mixture of 6CHBT and phenyl isothiocyanate, and doped with Fe_3O_4 particles, coated with oleic acid.

The structural transitions in ferronematic samples were indicated by capacitance measurements in a capacitor with anti-parallel ITO-coated glass electrodes (LINCAM co.). The capacitor with the anti-parallel alignment of glass electrodes with area approximately 1cmx1cm was connected to a regulated thermostat system. The temperature was stabilized with the accuracy of 0.05ºC. The distance between the electrodes (sample thickness) was D =5μm. An electric field was applied perpendicular to the surface of electrodes and a magnetic field was applied perpendicular to the electric field. The capacitance was measured at the frequency 1 kHz by the high precision capacitance bridge Andeen Hagerling with accuracy up to aF. The stability of the samples in strong magnetic fields was verified by repeating the capacity measurements after 3-5 months on the same samples, with reproducible results.

3 RESULTS

3.18CB-based ferronematics

The observations of the structural transitions in external field can be used for the determination of the type of anchoring of nematic molecules on magnetic particles surfaces. In our previous works [11-13] different types of structural transitions (in magnetic, electric or combined fields) in 8CB-based ferronematics were studied and it was shown that initial orientation of the magnetic moment of magnetic naoparticles and director of molecules of liquid crystal is perpendicular. In this paper we present the results of the investigation of electric Freedericksz transition in this ferronematic in strong bias magnetic field. By means of the Burylov and Raikher's expression for the free energy of ferronematic [7] the formula for the critical voltage was derived as follows

$$U_{FN}^2 = U_{LC}^2 + \frac{D^2}{\varepsilon_0 \varepsilon_a}\left(\frac{\chi_a B_b^2}{\mu_0} - \frac{4\mu_0 W^2 \phi}{M_s B_b d^2}\right) \qquad (2)$$

where $U_{LC} = (\pi^2 K_1/\varepsilon_0\varepsilon_a)^{1/2}$ is the critical voltage of electric Freedericksz transition in pure liquid crystal, K_1 is corresponding Frank orientation-elastic modulus of liquid crystal, ε_a and χ_a are the anisotropies of the dielectric permittivity and diamagnetic susceptibility of liquid crystal, respectively, D is the thickness of the ferronematic layer, Φ is the volume concentration of magnetic particles, M_s is the saturation magnetization of magnetic material, W is surface density of anchoring energy and d is typical size of magnetic particle. Following Eq. (2) the decrease of the critical voltage U_{FN} with increasing volume concentration Φ and its increase with increasing magnetic field B_b were expected.

The critical voltage of electric Freedericksz transition in pure 8CB (at B_b=0) was found to be U_{LC} = 0.86V. Following Eq.(2), the combination of B_b and Φ , at which leads to U_{FN}=U_{LC} , is for B_b=4T and Φ =5.10^{-4}. The surface density of anchoring energy calculated for these values is W=8.9 · 10^{-4} N/m. The critical voltages U_{FN} measured in 8CB-based feronematics with different volume

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concentration of magnetic particles Φ, at applied bias magnetic field B_b=4 T and for sample with volume concentration Φ =5.10^{-4} for different bias magnetic fields are summarized in Table 1. The application of strong constant bias magnetic field $B_b \parallel n$ leads to the violation of the initial $m \perp n$ condition. As was expected, the decrease of critical voltage with increased volume concentration of magnetic particles was observed and increase of critical voltage with increasing bias magnetic field, that confirmed perpendicular initial condition. The value of the surface density of anchoring energy, calculated by means of Eq.(2), was W~10^{-3} N/m, that corresponds to ω ~1.9. These values indicate soft or some intermediate state between soft and rigid anchoring of liquid crystal molecules on magnetic particles surfaces in studied ferronematic.

B_b=4T				
Φ	5.10^{-4}	8.10^{-4}	1.10^{-3}	2.10^{-3}
U_{FN} [V]	0.86	0.65	0.50	0.25
Φ=5.10^{-4}				
B_b[T]	4	6	8	12
U_{FN} [V]	0.86	2.30	3.50	5.80

Table 1: The critical voltages U_{FN} measured in 8CB-based ferronematic with different 6CHBT-based ferronematics

3.26CHBT-based ferronematics

The same type of structural transition was investigated also in the 6CHBT-based ferronematic. The obtained results are summarized in Table 2. In this case, the critical voltages increases with increasing volume concentration of magnetic particles Φ.

Sample		6CHBT	Φ=10^{-5}	Φ =10^{-4}	Φ=2.10^{-4}
U_{FN}[V]	B_b = 0T	1.050	1.051	1.053	2.035
	B_b = 2T	1.047	1.218	1.477	2.350
	B_b = 5T	1.895	1.990	2.121	2.765
	B_b = 8T	2.788	2.809	3.019	4.139
	B_b=11T	3.347	3.450	3.623	4.470
	B_b=15T	4.203	4.264	4.568	5.295

Table2: The critical voltages U_{FN} measured in 6CHBT-based ferronematic with different Φ at different B_b.

This could be understood as a demonstration of the soft anchoring with $\boldsymbol{m} \parallel \boldsymbol{n}$ boundary condition. In this case, the strong magnetic field does not violate, but stabilizes the favored $\boldsymbol{m} \parallel \boldsymbol{n}$ anchoring. This way the presence of magnetic admixture shifts the electric threshold field to higher values.

The presence of the $\boldsymbol{m}_0 \parallel \boldsymbol{n}_0$ boundary condition in the 6CHBT-based ferronematic was verified also by the investigation of the magnetic Freedericksz transition byexperiments, in which first the electric Freedericksz transition was invoked by strong bias electric field oriented perpendicular to the initial orientation of molecules of liquid crystal and then the increasing magnetic field $\boldsymbol{B}$ turns the nematic molecules, held by strong constant electric field $\boldsymbol{E}_b$, back to their initial planar orientation. As is shown in Table 3., the magnetic threshold decreases with increasing volume concentration of magnetic particles. These results verify the presence of the $\boldsymbol{m} \parallel \boldsymbol{n}$ boundary condition in the 6CHBT-based ferronematic.

Sample		6CHBT	Φ=10^{-5}	Φ=10^{-4}	Φ=2.10^{-4}
B_{FN}[T]	U_b=4.15V	6.413	2.988	2.467	1.823
	U_b=4.84V	11.403	4.432	3.415	2.138
	U_b=5.53V	12.348	7.189	4.660	2.388
	U_b=6.22V	13.327	10.154	6.784	4.775

Table 3: The critical magnetic fields B_{FN} measured in 6CHBT-based ferronematic with different Φ at different bias voltages.

3.3Ferronematics droplets

The prepared solutions of 6CHBT and phenyl isothiocyanate doped with fine magnetic particles were observed by polarizing microscope. The phase diagram of the sample with volume concentration of magnetic particles Φ =1.10^{-4} is shown in Figure 2.

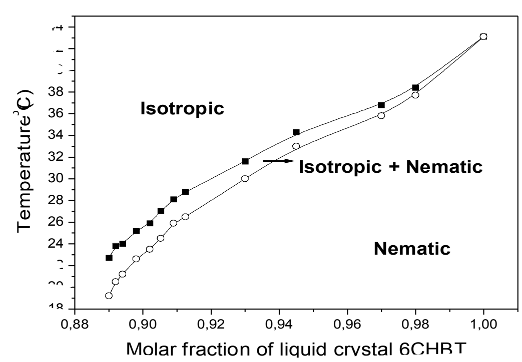

Figure 2: The phase diagram of the mixture of 6CHBT and phenyl isothiocyanate doped with fine magnetic particles (Φ=1.10^{-4}).

The created droplets were magnetically active and their sizes could be easily controlled by the change of the temperature. The Figure 3 shows the sample with molar fraction of liquid crystal X=0.906 and Φ=1.10^{-4} at temperatures t_1=26ºC (Fig.3a) and t_2=25ºC (Fig.3b). The droplet size increases with decreasing temperature.

Based on the above mentioned results obtained for the 6CHBT-based ferronematic, the $\boldsymbol{m} \parallel \boldsymbol{n}$ boundary condition was supposed also in the ferronematic droplets. Thus, the decrease of the critical magnetic fields with increasing volume concentration of magnetic particles was expected and also verified by the capacitance measurements.

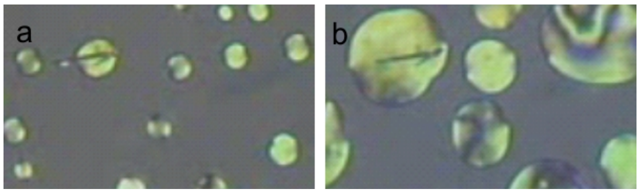

Figure 3: The ferronematic droplets observed at (a) t_1=26°C and (b) t_2=25°C (b) in the sample with molar fraction of the 6CHBT X=0.906 and volume concentration of magnetic particles Φ =1.10^{-4}.

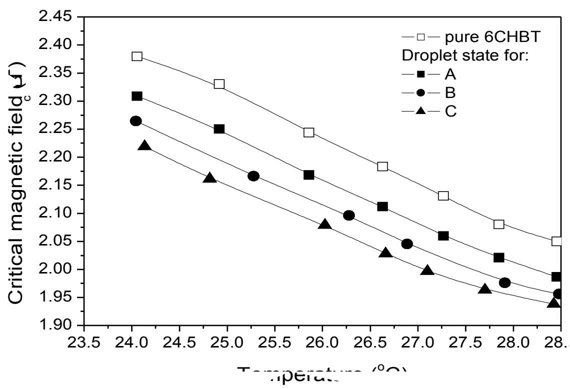

Figure 4:The temperature dependences of critical magnetic fields of pure 6CHBT, 6CHBT dissolved in phenyl isothiocyanate (X=0.906) (curve A), 6CHBT dissolved in phenyl isocyanate doped with Fe_3O_4 nanoparticles with volume concentration Φ_1=2.10^{-5} (curve B) and Φ_2=1.10^{-4} (curve C).

The temperature dependences of measured critical magnetic fields, obtained for the nematic phase of pure 6CHBT and 6CHBT (X=0.906) dissolved in phenyl isothiocyanate without magnetic particles (curve A) and for samples doped with magnetic nanoparticles (X=0906, Φ_1=2.10^{-5} and Φ_2=1.10^{-4}, curve B and C, respectively) are presented in Fig45. As it is seen, the critical fields of magnetic Freedericksz transition, found for the droplets in 6CHBT dissolved in phenyl isocyanate are lower than those measured in the nematic phase of the same sample. It is also obvious, that the presence of magnetic admixtures lowers the threshold of magnetic Freedericksz transition, what confirms the presence of $\boldsymbol{m_0} \parallel \boldsymbol{n_0}$ boundary condition in 6CHBT-based ferronematic droplets.

The structural transitions in ferronematics based on different thermotropic nematics 8CB and 6CHBT and in ferronematic droplets were investigated. Using the capacitance measurements, the dependences of the critical fields on the volume concentrations of magnetic particles, the boundary conditions between $\boldsymbol{m}$ and $\boldsymbol{n}$ were found: $\boldsymbol{m} \perp \boldsymbol{n}$ in the 8CB-based ferronematic and $\boldsymbol{m} \parallel \boldsymbol{n}$ in the 6CHBT-based ferronematics.

The magnetically active ferronematic droplets were firstly observed in the mixture of 6CHBT with fine magnetic particles and phenyl isothiocyanate. We suppose, the magnetic particles play the role of natural nucleation centres for the nematic droplets in isotropic phase.

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