Dynamics of Flat Barium Hexaferrite Particles in a Lyotropic
Liquid Crystal

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Abstract. This paper describes the results of experiments on the magnetization of barium
hexaferrite particles embedded in lyotropic liquid crystals. The carrier liquid crystal medium was
an aqueous solution of a mixture of sodium lauryl sulfate and lauric acid in a ratio 2/1. Barium
hexaferrite particles were stabilized with two layers of surfactant. The first layer consisted of
oleic acid molecules. Second layer was a mix of sodium lauryl sulfate and lauric acid in a ratio 1/1.
The process of particle magnetization was investigated by observing the effect of birefringence. The intensity of light passing through the system of crossed polaroids and the time
of its establishment were measured depending on the magnitude of the magnetic field and the
concentration of the components of the liquid crystal. It was found that the field dependence of
the birefringence effect changes significantly depending on the concentration of the liquid
crystal. In a concentrated solution in the liquid-crystalline phase, a significant enhancement of
the birefringence effect is observed in weak fields. As the concentration of the solution decreases,
the field dependence of the birefringence effect smoothly transforms into the curve for particles
dispersed in water.

1. Introduction
In 1970 F. Brochard and P.G. de Gennes [1] proposed the idea of imparting strong magnetic properties
to liquid crystals by dispersing ferromagnetic particles in them. By that, another way to control liquid
crystal ordering by means of a magnetic field would be obtained. Also, in this work the term for a new
object of research was proposed by obvious combination of two parts: ferro and name of corresponding
liquid crystal. Almost immediately an attempt was made to implement the proposed idea [2].
Unfortunately, it turned out that ferromagnetic particles stabilized by known methods (a layer of
surfactant or an electrical double layer) were poorly compatible with thermotropic liquid crystals. The existence of ferroLCs was possible only for a short time and only in very thin layers (tens, maximum
hundreds of microns) [3-6].

Experiments with ion-stabilized particles dispersed in an aqueous solution of a mixture of potassium
laurate and decanol-1 were more successful [7]. At certain concentrations of the component the solution
exhibits lyotropic liquid crystal properties. In [7] dispersions of iron oxide particles, stable in
macroscopic volume (order of centimeters) and capable to exist for a long time, were obtained. The
dispersed particles had a shape close to spherical. This circumstance makes orientation interaction of
the particles and liquid-crystalline matrix very difficult, if not impossible. Apparently therefore the
question of controlling the liquid crystal ordering by means of a magnetic field was not considered at
all in [7].

More recently, magnetic liquids based on barium hexaferrite particles stabilised in water by a double
layer of lauric acid molecules and sodium dodecyl sulphate have been synthesised [8]. Based on
measurements of their dynamic properties, it was concluded that the particles are disc-shaped with the
orientation of magnetic moment normal to the disc plane. The disk-shaped magnetic particles provide
an excellent opportunity to control the structure of liquid crystals with the help of magnetic field. It only
remains to find a suitable liquid crystal matrix compatible with these particles.

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In the present work the results of studies of remagnetization of barium hexaferrite particles in a concentrated solution of sodium dodecyl sulphate and lauric acid mixture are described. Under certain conditions micellar ordered structures are formed in such a solution. The uniform composition of the particle shells and the liquid crystal medium ensures their complete compatibility and stability.

2. Synthesis of barium hexaferrite particles
Flat particles of barium hexaferrite were prepared according to the hydrothermal method described in [9, 10]. To 40 ml of initial aqueous solution of 0.05 M iron nitrate Fe(NO₃)₃, and 0.01 M barium nitrate Ba(NO₃)₂ was added 40 ml of 2.72 n alkali solution under intensive stirring. The resulting suspension of iron hydroxide Fe(OH)₃ in a strong alkaline medium was placed in an autoclave. The reaction mixture was heated to 160°C at a heating rate of 3°C min⁻¹, kept at this temperature for 2 h, cooled to 100°C, then removed from the oven and cooled to room temperature.

The synthesized particles were then coated with surfactant. For this purpose the barium hexaferrite precipitate was suspended in 1-2% aqueous ammonia solution and then 0.1 g of oleic acid was added. The mixture was heated under stirring until the acid was completely dissolved and boiled for 10 min to remove excess ammonia. 1 M hydrochloric acid was added until a pH ≈ 3. The paste-like precipitate containing coated particles and excess oleic acid was separated, washed with deionised water and dried in an oven at 105°C. The paste was suspended in n-octane and boiled for better adsorption of the surfactant. After removal of the solvent, the precipitate was washed of excess acid with ethyl acetate. The precipitate was dried and peptized in petroleum ether. The small particles were peptized in the ether, while the larger ones coagulated and settled. An additional surfactant was chosen empirically for the coarse particles. The surfactant mixture contained equal molar fractions of sodium dodecyl sulphate (SDS) and lauric acid (LA). SDS was dissolved in water, the solution was heated to 50°C and LA was added while stirring. Large hydrophobic particles are peptized by a second surfactant layer with hydrophilic groups at the interface with the aqueous medium. The result is a stable aqueous-based ferrofluid. Figure 1 shows a schematic view of a particle stabilized by a double surfactant layer. The hydrocarbon tails are shown with lines and the polar groups are shown with circles - black in the case of oleic acid in the internal layer, light and black in the case of SDS and LA in external layer.

3. Barium hexaferrite particle size estimation
Evaluation of the particle size was done by measuring their magnetic properties in the isotropic phase of the solution. The procedure is well known and is called magnetogranulometric analysis. Unfortunately, low magnetic susceptibility of the sample did not allow us to perform analysis of the complete magnetization curve and to determine the parameters of particle size distribution [11]. Estimates were made of the average magnetic moment from the ratio of the susceptibility in a small magnetic field to the initial susceptibility. Assuming the Langevin law of particle magnetization, this ratio is equal:

\[ \frac{\chi(\xi)}{\chi(0)} = \frac{3}{\xi^2} - \frac{3}{s h(\xi^2)^2}, \quad \xi = \frac{Bm}{kT} \]

where \( \chi(\xi) \) and \( \chi(0) \) are the liquid's susceptibilities in weak field and without field, \( \xi \) - Langevin parameter, \( k \) - Boltzmann constant, \( T \) - absolute temperature.

Reduction of liquid's susceptibility with barium hexaferrite particles was \( \chi(\xi)/\chi(0) = 0.68 \) in field \( B = 1.4 \) mT. This corresponds to the value of Langevin parameter \( \xi = 1.5 \). Then the estimate of average magnetic moment would be \( m = 4\times10^{-18} \) Am². Setting the reference value of magnetization of barium hexaferrite to 380 kA/m, we get an estimate for average particle volume \( V = 10^{-21} \) m³. Average diameter for spherical particles is \( d = 30 \) nm. The obtained value looks quite realistic. Typical particle size in a standard magnetic fluid based on magnetite particles stabilized with oleic acid is 10 nm. Obviously, a double layer of surfactant can stabilize much larger particles.
Another possible way to determine the size of barium hexaferrite particles is to measure their dynamic properties. For this purpose the latter were peptized in a small concentration in an aqueous solution of 0.01 n dodecyl sulphate (Dispersion in pure water washes out the SDS from the stabilizing shells). The dynamic properties of the particles were measured using the effect of birefringence. The measuring scheme is standard. A helium-neon laser beam passes sequentially through a polarizer, a liquid sample in the electromagnet gap, an analyzer, and hits a photodiode. The output signal from the photodiode is measured with an eLockIn 203 synchronous amplifier (Anfatek). The electromagnet was fed with sinusoidal current of varying frequency. The magnetic field was oriented at an angle of 45 degrees to the plane of polarization of the laser beam. The output signal of the photodiode was measured at double frequency. Figure 2 shows a scheme of the experimental setup.

The photodiode output was measured as a function of frequency and amplitude of the alternating magnetic field. The concentration of magnetic particles was chosen in such a way that the intensity of the light was attenuated by a factor about e when passing through the sample. Under that condition, birefringence effect is maximal. Figure 3 shows the results of measurements of the intensity of transmitted light as a function of the magnetic field frequency. Measurements were made for two values of magnetic field amplitude 2.85 and 1.81 kA/m. The obtained curves have a classical Debye’s shape and are practically identical (they coincide after scaling with respect to the ordinate axis). The characteristic frequency of particle relaxation is about 200 Hz. A small slope at the beginning of upper curve can be attributed to coagulation of particles.

From the relaxation curve the relaxation time of particles and their average characteristic volume are determined:

\[ \tau_\ast = \frac{1}{2\pi f_\ast}; \quad V = \frac{\tau_\ast kT}{3\eta}; \]

where \( f_\ast \) is the field frequency at which the magnitude of the signal decreases by a factor of two, \( k \) is Boltzmann constant, \( T \) is the absolute temperature, and \( \eta \) is the viscosity of the carrier medium. From the analysis of the curves in Figure 3 it follows \( \tau_\ast = 8 \times 10^4 \) s. Then the volume of the particle \( \sim 10^{-21} \) m\(^3\), and the average diameter assuming spherical shape will be \( \sim 120 \) nm.

This value is distinctly greater than the diameter obtained from magnetic measurements. The difference is due to the fact that the Debye’s relaxation time is determined by the hydrodynamic size of the particles including stabilization shells. There is also a non-magnetic layer on the surface of the particles with a thickness of the order of one lattice period. Another factor that we do not take into account is nonspherical form of particles. This factor can increase time of relaxation by almost an order of magnitude. Unfortunately, we do not know the formfactor of our particles. Taking these circumstances, the difference in particle sizes obtained by different methods looks less significant.
Figure 3. Output voltage of photodiode as function of the magnetic field frequency. Measurements were made for two values of magnetic field amplitude 2.85 and 1.81 kA/m.

Figure 4. Output voltage of photodiode as function of the magnitude of magnetic field. Frequency of measurements equal to 40 Hz.

The birefringence effect was also measured as a function of the magnetic field strength. The results are shown in Figure 4, where the curve has a slightly inflected shape. In this case the magnitude of the birefringence effect is clearly determined by the orientation of anisotropic barium hexaferrite particles. The situation changes considerably if the particles are oriented by the field in a liquid crystal medium.

4. Relaxation of barium hexaferrite particles in a liquid crystal

As mentioned above, a concentrated solution of a mixture of sodium dodecyl sulphate and lauric acid was used as a liquid crystal carrier medium. The SDS/LA molar ratio was chosen to be 2:1. The concentration of the solution was gradually increased until the system reached an ordered state. Its onset was monitored by observing the transparency of the cuvette in polarized light.

The viscosity of the liquid crystal was several orders of magnitude higher than that of water. This made measurements with alternating sinusoidal fields practically impossible. A rectangular alternating field with a frequency of 0.1 Hz was chosen. By changing the field to the opposite value, the magnetic particles are reoriented and, accordingly, the intensity of the light passing through the polaroid system changes. The signal was in the form of an inverted bell with a slowly decaying tail. The amplitude of the bell determined the magnitude of the birefringence effect, and its position determined the characteristic reorientation time of the barium hexaferrite particles. Figure 5 shows a qualitative view of the signal at the photodiode output.

Figure 6 shows the results of measuring the intensity of the transmitted light and the time of its establishment as a function of the magnetic field. First of all, it is noteworthy that the field dependence of the intensity has a qualitatively different appearance - the curve is much more convex. That is, the liquid-crystalline medium enhances the birefringence effect in weak fields.

Dependences of reorientation time and birefringence signal amplitude on magnetic field magnitude at lower matrix concentrations were measured. The results of measurements are presented in Figure 7. Although the carrier medium is no longer in an ordered state, the field dependence of the birefringence effect is still qualitatively different from that for particles suspended in water. Moreover, the field dependence curves gradually converge as the liquid crystal concentration decreases. Apparently, the interaction of planar barium hexaferrite particles with the surrounding micelles is more complex than simple steric repulsion.
5. Conclusion

Disc-shaped particles of barium hexaferrite were synthesized by the method of thermal decomposition. Estimates of the average particle size are made basing on measurements of their magnetic and dynamic properties. The dependence of the birefringence effect on magnetic field magnitude has been measured for particles suspended in water.

The field dependences of the birefringence effect and the time of reorientation of particles in a lyotropic liquid crystal, a concentrated solution of a mixture of sodium dodecyl sulfate and lauric acid, have been measured. A significant qualitative difference from the field dependence of the birefringence effect for particles in water was found.

The field dependence of the birefringence effect has been measured for particles in liquid crystal solutions of lower concentrations. Despite the absence of an ordered liquid-crystalline state, the curves obtained also differed from the curve for particles in water. With a decrease in concentration, the obtained dependences gradually approach the curve for pure water.

Figure 5. Example of photodiode output signals during remagnetisation of barium hexaferrite particles in liquid crystal.

Figure 6. The intensity of the transmitted light and the time of its establishment as a function of the magnetic field.

Figure 7. Intensity of the transmitted light as a function of magnetic field strength. The upper curve corresponds to half of initial concentration. The middle curve corresponds to a quarter. Bottom curve corresponds to water.
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