

# Water-based ferrofluids for biomedical applications: physical characterisation

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Magnetic nanoparticles offer some attractive possibilities in biomedicine, and the biocompatible ferrofluids led to a range of new biomedical and diagnostic applications. We have prepared 2 sorts of water-based ferrofluids and then we have made a physical characterization of these. Thus, we have determined the size distributions of particles in ferrofluids by a dynamic light scattering (DLS) method and by analyzing the magnetization curves of ferrofluids. Then we have analyzed the magneto-optical properties (linear dichroism and linear birefringence) in the ferrofluids, using a method relied on the measurement of the azimuthal distribution of the transmitted light through a homogenous ferrofluid film magnetized parallel to its plane by an external continuous magnetic field.

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## 1. Introduction

Ferrofluids are colloidal suspensions of superparamagnetic nanometer sized particles in a suitable liquid carrier [1, 2]. The recent development of biocompatible functionalized ferrofluids led to a range of new biomedical and diagnostic applications [3–6]. A lot of research was conducted to develop carriers for drug delivery and drug targeting designed for in vivo usage.

For the successfully guidance of magnetic carriers through capillary vessels and tissues by using magnetic fields applied from the exterior, it is important to prevent the particles' spatial structuring.

In the presence of magnetic field the ferrofluids becomes anisotropic. Their anisotropy is manifested on the dependence of the mechanic, electric, magnetic and optical properties on the direction and the intensities of the magnetic field applied. The analysis of the magneto-optical properties (linear dichroism and linear birefringence) in the ferrofluids is a way to emphasize and evaluate the structuring of ferrofluids in the presence of magnetic field [7-9].

Synthesis and rheological properties of an aqueous ferrofluid consisting of Fe<sub>3</sub>O<sub>4</sub> ultrafine particles stabilized by citric acid have been described in [10]. AFM study in [11] shown that claim and aggregated particles are related to ferrofluid stability.

In this work we present the method of preparation of two sorts of aqueous ferrofluids. Also we have made a physical characterization of these ferrofluids and we have analyzed the magneto-optical properties (linear dichroism and linear birefringence) in the ferrofluids, measuring the azimuthal distribution of the transmitted light through a thin film of homogenous ferrofluid in the presence of an applied magnetic field.

Magneto-optical measurements were used to evaluate the stability and the structuring reversibility of the

magnetic colloids subjected to static magnetic fields. The dosage of the surfactants was found to have an important effect on increasing the solid content and magneto-optical behaviour.

## 2. Experimental

### 2.1. General comment

Two sorts of ferrofluids were prepared. For *sort 1*, the magnetite particles were prepared in-situ precipitation in a polyethylene glycol (PEG) solution and then the particles was covered with oleate sodium as a primary layer, followed by covering with polyethylene glycol. For *sort 2*, the magnetic particles were prepared by a precipitation technique and the water-based ferrofluid was prepared by coating the particles with oleate sodium as a primary layer, followed by covering with polyethylene glycol (PEG).

### 2.2. The water based ferrofluids obtained by in-situ precipitation of magnetite particles

A Fe<sup>2+</sup> : Fe<sup>3+</sup> acid solution of 1 : 2 molar ratio was added over a 13.33 % PEG<sub>2000</sub> solution. In a NaOH diluted solution, at 60-70<sup>o</sup> C was added in the same time the PEG – Fe<sup>2+</sup>/Fe<sup>3+</sup> salt and 4 % NaOH solutions. After 30 minutes of ultrasonication, the magnetite precipitated in-situ was washed several times with distilled water; in the last washing water was added a 0.01 M HCl solution until the pH reached 5.5-6 value. The magnetite suspended in distilled water was treated with a 13.2 % sodium oleate solution and ultrasonated 30 minutes at 70<sup>o</sup> C. After that, a 78.5 % PEG<sub>2000</sub> solution was added and ultrasonated 30 minutes at 45 °C. Finally, the sample was treated with a 0.01 M HCl solution until the pH = 7, then ultrasonated again for 5 minutes. It was obtained a very stable

ferrofluid, being homogenous for > 120 days. The clear supernatant was then collected for analysis

### 2.3. The water based ferrofluids obtained by a precipitation technique

1 g magnetite was washed and suspended in a 0.01 M HCl solution. In this suspension was adding 15 ml of aqueous poly (ethylene glycol) 2000 (PEG<sub>2000</sub>) and sodium oleate solution. The sample was ultrasonated 10 minutes at 70 – 90 °C. After repeated washings with distilled water, a 20 % PEG<sub>2000</sub> solution was added over the suspension. This sample was ultrasonated again 10 minutes at 45 °C. It was obtain a ferrofluid that became non-homogenous after a week. The clear supernatant was then collected for analysis

### 2.4. Ferrofluids characterization

The size distributions of particles in the supernatant fluids were determined by a dynamic light scattering method (DLS) and by analyzing the magnetization curves of ferrofluids [10, 11]. The magnetization curves were obtained using a balance force method.

### 2.5. Magneto-optical analysis technique

Elliptically polarized transmitted light results when a linearly polarized light is incident normally to a ferrofluid film subjected to an external magnetic field parallel to the plane of the film. This phenomenon is a result of linear birefringence and is known as the Cotton-Mouton (C-M) effect. Also, as a result of linear dichroism, the transmission axis of the transmitted light is rotated by an angle with respect to that of the incident light, phenomenon known as the C-M rotation.

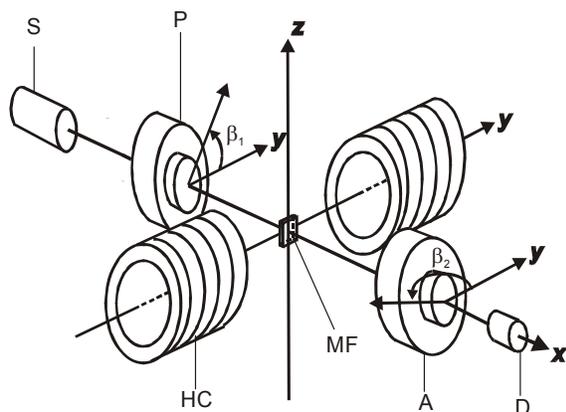


Fig. 1. The experimental set-up for the study the azimuthal distribution of the transmitted light intensity.

For a qualitative analysis of the two effects we have adopted a method relied on the measurement of the

azimuthal distribution of the transmitted light intensity through a homogenous ferrofluid film magnetized parallel to its plane by an external continuous magnetic field [14, 15]. The experimental set-up is shown in Fig. 1. A He-Ne laser beam ( $\lambda=632$  nm) is linearly polarized by the polarizer P and then is incident normally to the ferrofluid film MF. The magnetic field is generated by a pair of Helmholtz coils HC and applied to the ferrofluid film perpendicular to the propagation direction of the light. The angle  $\beta_1$  between the transmission axis of the polarizer and the applied magnetic field can be adjusted by rotating the Helmholtz coils. The analyzer A is used to examine the polarization state of the transmitted light through the ferrofluid film. The azimuthal angle  $\eta=\beta_2-\beta_1$  (the angle between the two transmission axis of the analyzer and the polarizer) is modified rotating the transmission axis of the analyzer with the aid of a stepping motor, driven by a PC with a step angle of 2°. Finally, a receiving photodiode (D) is used to detect the intensity  $I$  of the transmitted light through the sample. The signals from photodiode are transmitted to a data acquisition board in a PC for storage and processing.

In this work the  $I - \eta$  curves were measured at  $\beta_1=45^\circ$  and various  $H$ 's. Under zero field, the symmetric  $I - \eta$  curves exhibits a relative maximum intensity at  $\eta_{I=max}=0$  and zero intensity at  $\eta_{I=min}=90^\circ$  and  $-90^\circ$ . The symmetric  $I - \eta$  curves under  $H \neq 0$  were also obtained with a translational shift  $\Delta\eta$  with respect to the zero field curve. This shift implies that the transmission axis of the transmitted light was rotated by an angle  $\Delta\eta$  with respect to that of the incident light (i.e. C-M rotation), and it is considered as a qualitative measure of the linear dichroism. On the other hand, the minimum intensity  $I_{min}$  occurred at  $\eta_{I=min}$  is non-zero under  $H \neq 0$ . This  $I_{min} \neq 0$  implies that the transmitted light is not linearly but elliptically polarized, and it is considered a qualitative measure of birefringence.

Magneto-optical measurements were used to evaluate the stability and the structuring reversibility of the magnetic colloids subjected to a static magnetic field.

## 3. Results and discussion

### 3.1. Ferrofluids synthesis and characterization

The magnetization of saturation obtained from the magnetization curve (Fig. 2 and Fig. 3) is 36,6 Gs (2.928 kA/m) for the *sort 1* ferrofluid, and 46.7 Gs (3.736 kA/m) for the *sort 2* ferrofluid respectively. The *sort 1* ferrofluid was very stable, being homogenous for > 120 days, and the *sort 2* ferrofluid had poor stability and became non-homogenous after a week because of the lower quantities of the PEG<sub>2000</sub> solution.

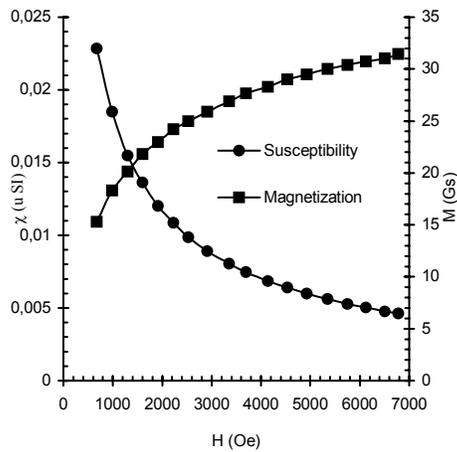


Fig. 2. Magnetization curve obtained using a balance force method for sort 1 ferrofluid.

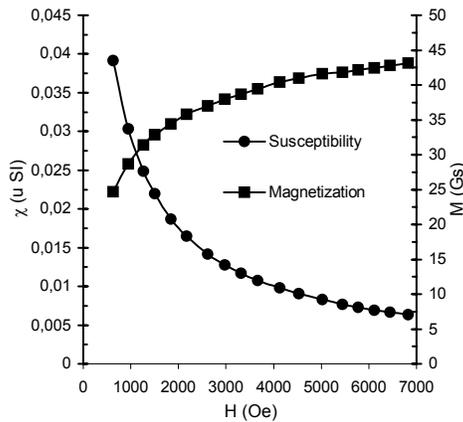


Fig. 3. Magnetization curve obtained using a balance force method for sort 2 ferrofluid.

Fig. 4 presents the particle size distribution obtained by DLS method for the *sort 1* ferrofluid. The particle size distribution is a lognormal function and the average size of the magnetic particles from the suspensions is 115 nm.

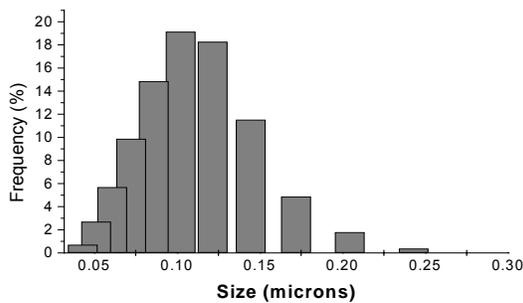


Fig. 4. Particle size distribution determined by DLS for the *sort 1* ferrofluid.

Fig. 5 presents the particle size distribution obtained by DLS method for the *sort 2* ferrofluid. The particle size

distribution is a lognormal function and the average size of the magnetic particles from the suspensions is 140 nm.

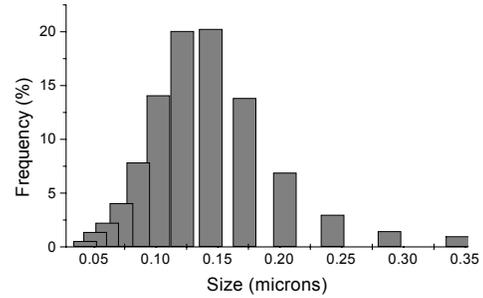


Fig. 5. Particle size distribution determined by DLS for the *sort 2* ferrofluid.

It is evident that the magnetite particles precipitated flocculate rapidly and this process determines the instability of the *sort 2* ferrofluid.

### 3.2. Azimuthal distribution of transmitted light intensity

As we emphasized above, to obtain the most significant variation in the polarization of the incident light through the ferrofluid, the angle  $\theta$  between  $H$  and the polarization of the incident light is set to be  $45^\circ$ . For  $H = 0$ , the  $I-\eta$  curve was symmetric with zero intensity at  $\eta = 90^\circ$  and  $-90^\circ$ . The symmetric  $I-\eta$  curves were also obtained with a translation shift by a  $\Delta\eta$  ( $\equiv \eta_{I=\min}(H) - \eta_{I=\min}(H=0)$ ) with respect to the zero field curve.

In Fig. 6 are shown the  $I-\eta$  curves for the *sort 1* ferrofluid. To decide the  $\Delta\eta$  precisely the  $I-\eta$  curves at  $\eta$  around  $-90^\circ$  were enlarged. Increasing the intensity of magnetic field up to 600 Oe (48 kA/m), the  $I-\eta$  curves are moved and the  $\Delta\eta$ 's values increased gradually up to  $4^\circ$ . The variation in  $\Delta\eta$  may be attributed to the periodic long chain structures, which are formed in the ferrofluid film plane. The minimum intensity  $I_{\min}$  occurred at the  $\eta_{I=\min}$  was found to be nonzero under  $H \neq 0$  and increased as raising  $H$ .

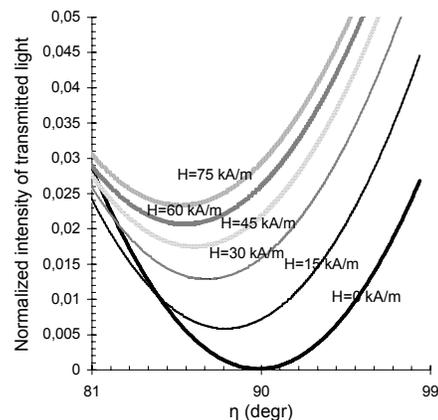


Fig. 6. Azimuthal distribution of the transmitted light intensity for the *sort 1* ferrofluid.

The existence of  $I_{min} \neq 0$  suggests that the transmitted light is not linearly but elliptical polarized under magnetic fields. The fact that  $I_{min}$  depends on the magnetic field intensity implies that the configuration of the elliptical polarized transmitted light is affected by the applied magnetic field. Long chains of particles are formed in the ferrofluid film plane. Increasing the field intensity, these long chains move closer to each other, thus changing the spatial anisotropy of the ferrofluid film.

In Fig. 7 are shown the  $I$ - $\eta$  curves for the *sort 2* ferrofluid. The  $\Delta\eta$ 's values increased gradually up to  $6.8^\circ$  as  $H$  increased to 300 Öe (24 kA/m). A similar behavior is observed for  $I_{min}$ . Increasing the intensity of field up to 600 Öe (48 kA/m), the value of  $\Delta\eta$ 's increased gradually, but the minimum intensity  $I_{min}$  occurred at the  $\eta_{I=min}$  decreased gradually as raising  $H$ . This significant variation in  $\Delta\eta$  may be attributed to the periodic long chain structure, which is formed in the magnetic fluid film, and it is considered as a qualitative measure of the linear dichroism. The minimum intensity  $I_{min} \neq 0$  occurred at  $\eta_{I=min}$  under  $H \neq 0$ , implies that the transmitted light is not linear but elliptical polarized under magnetic fields, and it is considered a qualitative measure of birefringence.

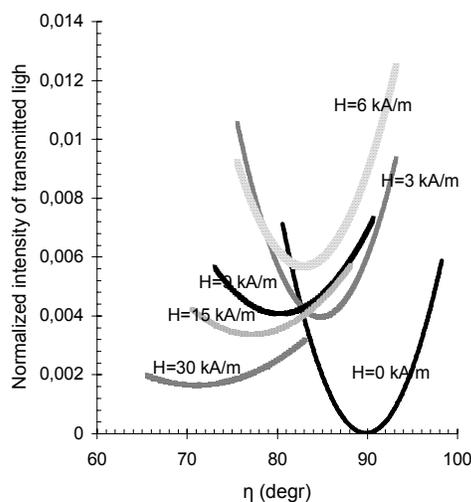


Fig. 7. Azimuthal distribution of the transmitted light intensity for the *sort 2* ferrofluid.

The decreased value of  $I_{min}$  under magnetic field with intensity more than 300 Öe (24 kA/m), are attributed to the dosage of the surfactant for the *sort 2* ferrofluid. Because of the lower quantities of surfactant in the *sort 2* ferrofluid, appears the physical processes that conduct to the transformation of the ellipticity of the transmitted light and the stability of the ferrofluid is diminished. Thus, the transmitted light is no more elliptical polarized but is transformed in a circular polarized transmitted light.

#### 4. Conclusions

In this paper we have presented some recent efforts devoted to the preparation and physical characterization of water based ferrofluids for biomedical applications.

Magneto-optical measurements were used to evaluate the stability and the structuring reversibility of the magnetic colloids subjected to static magnetic fields. The dosage of the surfactants was found to have an important effect on increasing the solid content and magneto-optical behavior.

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