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Field-induced flocculation on biocompatible magnetic colloids

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Abstract

Field dependence of the optical transmission of a polyaspartic-coated magnetite magnetic fluid dispersed in water was investigated at different particle volume fractions. The particle size distribution of the sample was obtained from the analysis of the transmission electron microscopy pictures. The transmissivity decreased increasing the magnetic field until a critical field is achieved. Above this value, the opposite effect was observed. Indeed, the critical field decreases the higher the particle volume fraction being in qualitative similarity with phase separation behavior. However, the origin of the effect is attributed to the precipitation of field-induced nanoparticle chains. These phenomena might be useful on obtaining one-dimensional nanoparticle arrangements.

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Keywords: Magnetic liquid; Fine particle system; Magneto-optical effect

1. Introduction

Magnetic nanoparticles have several technological applications ranging from magnetic recording media to cancer diagnosis and treatment [1–3]. The later is achieved using a biocompatible magnetic colloid [4], which consists of magnetic nanoparticles adequately coated to guarantee stability under physiological conditions. In this work, we investigated the magneto-optical property of a biocompatible magnetic colloid. Indeed the magneto-optical properties of magnetic colloids have been under study for more than 20 years [5–12]. Most investigations have been on magnetic birefringence. Optical transmission investigations, however, are rarer [7–9]. In this study, we investigated the field dependence of the optical transmission of a polyaspartic-coated, water-based, magnetite magnetic fluid sample as function of the particle volume fractions. The present study might have important applications on the arrangement of one-dimensional nanostructures [13].

The magnetic fluid sample was obtained following a procedure described in the literature [14]. Fig. 1 shows the sample particle size polydispersity profile obtained from the transmission electron microscopy (TEM) micrographs using a JEOL JEM-3010 ARP microscope operating at 300 kV (resolution 1.7 Å). A histogram was obtained from these pictures. The modal particle diameter ($d = 8.42$ nm) and the size dispersity (0.31) were obtained, assuming a lognormal distribution function. The particle volume fraction (ϕ) was calculated using $\phi = N\pi/6 \int D^3 P(D)\,\mathrm{d}D$, where N is the number of particles per unit volume obtained from atomic absorption analysis, and $P(D)$ is the particle diameter distribution. The inset shows a high-resolution TEM picture from which we found spherical-shaped nanoparticles.

2. Experimental setup

The room temperature magneto-transmissivity data were obtained using the traditional lock-in detection technique. The experimental setup consists of a chopped laser beam (632 nm) of 10 mW crossing perpendicularly the sample cell before illumination of the photo detector. The flat quartz sample cell has a sample thickness (L) of 1 mm. Both polarizer and analyzer are attached to a goniometer device that allows full angular rotation. The sample cell is

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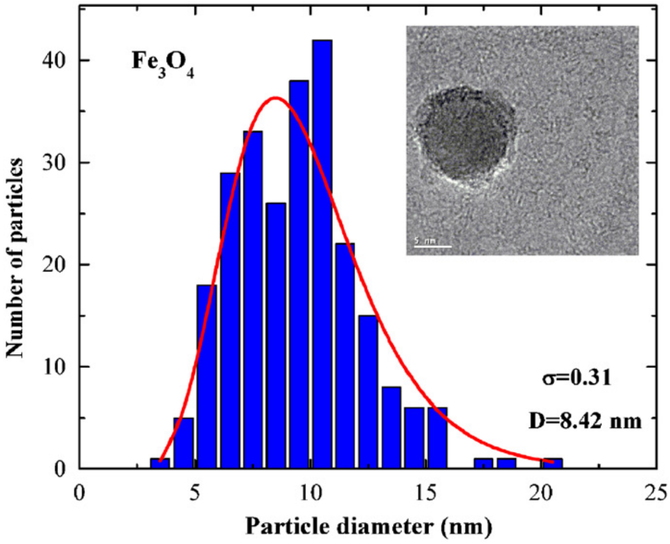

Fig. 1. Particle size distribution of the magnetite nanoparticles obtained from the transmission electron microscopy (TEM) pictures. The inset shows a high-resolution TEM picture.

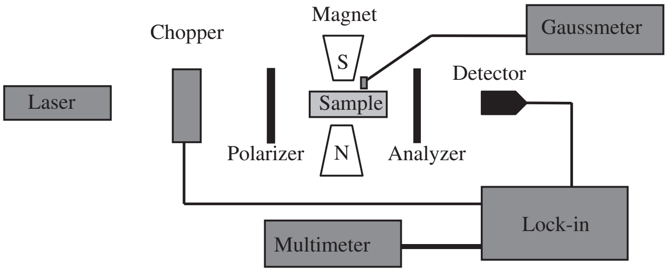

Fig. 2. Experimental setup of the magneto-transmissivity measurements.

mounted in the gap of an electromagnet so that the laser beam and the external magnetic field are mutually perpendicular. The axes of the polarizer and analyzer are set parallel to the magnetic field direction. Also, an absorption filter is positioned before the polarizer with the objective of decreasing the light transmission and avoiding thermodiffusion effects [15]. Fig. 2 shows the magneto-transmissivity experimental setup.

3. Theoretical model

The extraordinary rays (electric field parallel to the magnetic field) transmissivity of the sample has contributions from the absorption cross-section [7,8,16]:

$$\sigma_{\mathrm{abs}} = \frac{4\pi\sigma}{w[1 + \langle N\rangle(\varepsilon - 1)]^2}, \tag{1}$$

and also due to the scattering cross-section:

$$\sigma_{\mathrm{scat}} = \frac{4\pi^2 n_{\mathrm{c}} v(\varepsilon - 1)^2}{3\lambda_{\mathrm{e}}^3[1 + \langle N\rangle(\varepsilon - 1)]^2}, \tag{2}$$

where $\lambda_{\mathrm{e}} = \lambda/\sqrt{\varepsilon_{\mathrm{water}}}$ with λ, w, $\langle N\rangle$, ε, n_{c}, v, and σ, respectively, the laser wavelength, the laser frequency, the mean depolarization factor in the direction parallel to the magnetic field, the relative dielectric constant of the nanoparticle with respect to the solvent, the number of particles forming a linear chain, the particle volume, and the electrical conductivity of the nanoparticle or agglomerate. As a result, one can obtain for the transmissivity of extraordinary rays:

$$I = I_0 \exp\left(\frac{-2\pi L\phi(\sigma_{\mathrm{abs}} + \sigma_{\mathrm{scat}})}{\lambda}\right). \tag{3}$$

4. Experimental results and discussion

Fig. 3 shows the extraordinary transmissivity of a magnetic fluid sample with a particle volume fraction of 0.40% as a function of the magnetic field. The transmission decreases the higher the magnetic field value until a minimum is achieved, while above it the opposite effect is observed. According to the literature, the decrease of the transmissivity for higher field values is assumed to be a result of a decrease of the average depolarization factor as a function of magnetic field due to the field-induced formation of agglomerates, or because of the rotation of anisometric nanoparticles [7,8]. However, as far as we know, the opposite effect (namely the presence of a minimum) has not been reported in the literature yet.

Indeed the critical field depends on the particle volume fraction. Fig. 4 shows the extraordinary transmissivity for several magnetic fluid samples. Note that, as expected, the higher the particle concentration the lower the transmission at zero magnetic field. In addition, the critical field decreases the higher the particle volume fraction. This behavior is the same obtained when a phase separation

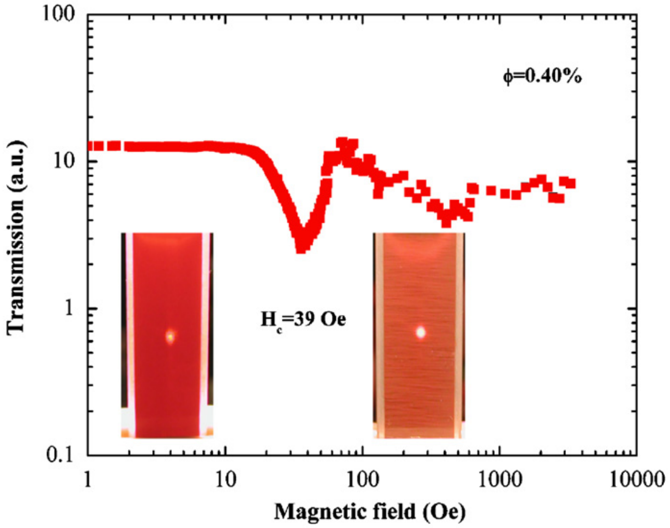

Fig. 3. Optical transmission as function of a magnetic field for a magnetic colloid sample with a particle volume fraction of 0.40%. Note the log–log scale. The inset shows the magnetic colloid sample before and after the critical field.

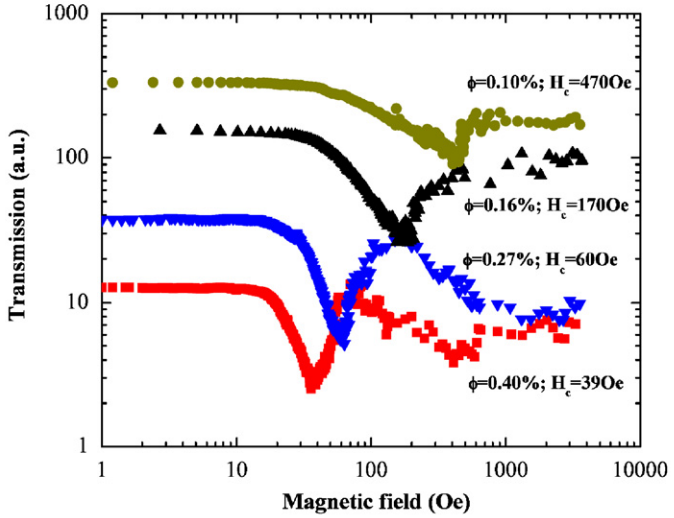

Fig. 4. Optical transmission as function of a magnetic field for magnetic colloid samples with different particle volume fractions. Note the log–log scale.

(reversible transition) occurs in the magnetic colloids, where a homogeneous system shows a transition to a bidisperse phase revealing droplets of highly concentrated colloidal particles [17–20]. Phase separation has been induced by decreasing the temperature, applying a magnetic field, or increasing the particle concentration.

Further, in order to prove the origin of this effect we obtained pictures from the magnetic colloid samples on different magnetic fields. The inset pictures of Fig. 3 show the magnetic colloid sample on different magnetic field conditions. On the left is shown the picture obtained on zero-field condition. One can observe that on this field the sample is homogeneous. However, on the right is shown a picture of the sample obtained near the critical field. One can observe long chains being formed in the magnetic field direction and more important the sample shows the precipitation of this long nanoparticle chains.

All the samples investigated showed a similar behavior. Therefore, we conclude that the minimum on the magneto-transmissivity measurement is related to the precipitation of field-induced nanoparticle chains. Other magnetic colloid samples with different particle sizes, coating layers, and/or liquid carriers are now under investigation and the results will be published elsewhere. On the other hand, we should point out that this phenomenon does not occur on pre-synthesized samples since the magnetic colloid stability has not been affected.

5. Conclusion

In conclusion, we had investigated the magneto-transmissivity of a biocompatible magnetic colloid. The transmissivity was shown to decrease the higher the magnetic field until a minimum was achieved; above this critical field value the opposite effect was observed. The phenomenon was attributed to the precipitation of field-induced nanoparticle chains, which might have interesting applications on controlling the arrangement of one-dimensional nanostructures.

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