Magnetic-field tunability of optical properties in colloidal suspensions of Goethite (α-FeOOH) nanorods

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Abstract

The dependence of polarized optical properties of colloidal suspensions of goethite (α-FeOOH) nanorods in water and PAO base fluids under the action of an applied magnetic field are investigated in the ultraviolet, visible and near infrared from 300 to 1500 nm wavelength. We found that the transmittance in the NIR range can be tuned by changing magnetic field direction and strength. Moreover, we found that the magnetic field dependence of optical properties is strongly connected to the base fluid where magnetic nanoparticles are suspended. The obtained results show that the optical properties of goethite-based suspensions are very sensitive to even weak external magnetic fields, with promising perspectives for sensing applications.

Keywords: goethite, NIR absorption tuneability, optical properties, optical extinction coefficient.

Introduction

Goethite (α-FeOOH) is a common ferric oxy-hydroxide in natural environment and so far has been extensively investigated for several applications including water purification [1], humidity sensing, organic pollutant degradation [2], coatings, pigments, lithium-ion batteries, as catalysts and for other applications, by virtue of its chemical stability, nontoxicity and low cost [3-8]. Magnetic nanoparticles are materials of biomedical interest thanks to their application in magnetic resonance imaging, hyperthermia for tumor treatment and drug delivery. Furthermore, Bellova et al. reported a new application of magnetic Fe3O4 nanoparticles in the treatment of amyloid diseases as inhibitors of formation of amyloid aggregates with the potential to destroy amyloid fibrils [9]. Goethite nanoparticles behave as an antiferromagnetic material [10] and have typically an elongated shape, forming nanorods of various sizes depending on the synthetic approach [11-13]. Sun et al. explored a method to control the shape of α-FeOOH nanocrystals based on precipitation from the hydrothermal reaction by adjusting the molar ratio of Fe3+ (or Fe2+) to SO42-. The authors reported that, for a constant concentration of metal ion, the shape of the product varies from rod-like nanocrystals to bundles and amorphous particles with increasing numbers of persulfate ions. [14].

Lemaire et al. widely investigated goethite-based colloids and demonstrated that they are mineral liquid crystals exhibiting peculiar magnetic properties [15-17]. In particular, goethite nanorods show different magnetic properties, by holding a permanent longitudinal magnetic moment along the elongated axis, probably due to uncompensated surface spins within the anti-ferromagnetic crystal
structure. These nanostructures also show a negative magnetic susceptibility, along the shortest particle dimension, leading to the formation of a lyotropic nematic phase that aligns in magnetic fields [18]. The optical nonlinearity of the material indicate possible applications in optical switching and frequency conversion elements in the telecommunication and information processing industries [19]. In fact, nanorods orient parallel to the field and reorient perpendicularly when the magnetic field passes a threshold [15,20,21]. Aqueous colloidal suspensions of goethite nanoparticles were investigated as potential liquid crystals because of the peculiar optical properties due to a magnetic-field induced birefringence, called “Majorana phenomenon” [16], related to the orientation of anisometric particles by the field. A net difference in absorption along the particle axes, i.e. dichroism, was observed, with the strongest absorption of polarized light parallel to the long particle axis. This behavior is very important in the view of applications of these fluids as liquid crystals, e.g. to tailor new types of materials by templates. A smectic phase on aqueous dispersions of goethite rods was identified also in extremely polydisperse systems [22]. Similarly, Reena Mary et al. investigated the light transmission properties of magnetic nanofluids of metallic nickel nanoparticles revealing the differential absorption for both parallel and perpendicular polarized light with respect to the field direction. They also reported that the dichroism disappeared when the field was removed in either polarization indicating the superparamagnetic properties of the particles [23]. The peculiar magnetic properties of these metallic nanofluids open the way to various photonic applications as optical devices controllable by an external magnetic field. The opportunity of tuning the transmittance of polarized light, mainly in the NIR range, by properly applying a magnetic field was also demonstrated in water based colloids and it was found dependent on the size of goethite nanorods [11]. Furthermore, a nematic phase, with its field-response properties, was observed also in colloidal suspensions of goethite in aprotic solvents as N-methyl-2-pyrrolidone and dimethylsulfoxide [24]. Moreover, a strong Kerr effect, that is a change in the refractive index of a material in response to an applied electric field, was also observed with isotropic goethite suspensions in these polar aprotic solvents [20]. However, an in-depth investigation of the dependence of polarized optical properties of colloidal suspensions of goethite nanorods under the action of an applied magnetic field has only partially been performed in water-based colloids, while has never been performed in other fluids such as in goethite suspensions in oils like polyalphaolefin (PAO), that could open to new applications. Therefore, in this work the dependence of polarized optical properties of colloidal suspensions of goethite nanorods in water and PAO based fluids under the action of an applied magnetic field are systematically investigated in the UV, visible and near infrared spectral regions, from 300 to 1500 nm wavelength.

**Experimental**

Goethite (α-FeOOH) nanorods have been synthesized by the aging of ferrihydrite suspensions obtained through co-precipitation. In the synthesis, Fe(NO₃)₃·9H₂O (99% pure, by Sigma-Aldrich) has been used as metal oxide precursor; NaOH (anhydrous pellets, by Carlo Erba) has been used to prepare co-precipitation solutions; deionized water (Millipore, Billerica MA, USA, 18.2 MU) was used as solvent. The nanorods were prepared by adding dropwise 5 mL of a 0.06 M solution of Fe(NO₃)₃ to 45 mL of a 1.5 M solution of NaOH at room temperature, leading to a ferrihydrate precipitate which was aged for three days at room temperature. After the ageing period, the obtained goethite precipitate has been washed several times with water followed by centrifugation. The details of this preparation route are reported into a previous publication [11]. The 0.1 wt% stable colloids in water have been obtained by proper dilution and 5 min ultrasound irradiation using a Sonics VCX130 (Sonics & Materials, Inc.) operating at 20 kHz and 130 W,
equipped with a 6 mm diameter Ti$_6$Al$_4$V alloy tip, operated at 70% power. Final pH was adjusted to 11 with NaOH. Details about the characterization of synthesized nanopowders by Powder X-ray Diffraction and Scanning Electron Microscopy, as well as the Dynamic Light Scattering (DLS) and ζ-potential measurements on the obtained water-based colloidal suspensions are reported in the same previous work [11].

For the suspension in oil, sodium docusate was used as surfactant. 0.086 wt% of sodium docusate (provided by Sigma-Aldrich) has been dissolved into a 0.01 vol% (0.043 wt%) goethite nanorods colloidal suspension in water. The suspension has been sonicated for 20 min at 40 °C into a sonication bath to better disperse the nanorods and favor the adsorption of sodium docusate on the surface of nanorods. The suspension has been stirred overnight. The goethite nanorods have been precipitated by centrifugation and dried at ambient atmosphere and 105 °C for 1 h. An adequate amount of PAO (poly alpha olefin, Sigma-Aldrich) oil has been added to the dry powder and sonicated into a sonication bath at room temperature for 15 min to obtain 100 mL of a 0.01 vol% stable suspension. The stability of PAO-based goethite suspensions was previously assessed [25] by means of DLS and ζ-potentials measurements.

Optical transmittances in the UV-Vis-NIR range from 300 to 1500 nm have been determined both in absence of an external magnetic field and under different magnetic field intensities and directions with respect to light polarization using a Perkin-Elmer Lambda900 spectrometer equipped with Glan-Thomson polarizers (Figure 1). The spectral resolution was 2 nm. Different values of magnetic field were created during optical measurements using permanent magnets. The magnetic field was measured using a Bell 640 Incremental Gaussmeter and a transverse probe 5 mm large and 1 mm thick. The probe was located at the point of optical measurements.

Figure 1: Schematics of experimental setup geometries used in the work. The direction of the optical beam (k vector of the electromagnetic wave) is fixed. The external magnetic field B can have two possible directions. Two combinations of the radiation electric and magnetic fields E and H are possible (black and green fonts in the picture), for a resulting overall number of three polarizations:

1) $B||k$, $E,H_|_B$;
2) $B_|k$, $E_|_B$, $H||B$;
3) $B_|k$, $E||B$, $H_|_B$.

Results and discussion

The goethite nanoparticles showed rod-like particles with length of about 300–500 nm and thickness of a few tenths nm, packed into nematic arrangement [11]. With the procedure described above, optimized stable suspensions in water and oil were achieved.

- **Goethite in water (F1)**

At first, we assessed the optical properties in the absence of external applied magnetic field. For diagnostic purposes, we carried out two different kinds of measurements: the first one with no
polarization selection at all and the second one selecting the linear polarization of the probe light beam. As expected, the obtained spectra were identical for the two perpendicular directions of linear polarization and also identical to unpolarized spectra. This confirmed the isotropic character of colloids in absence of magnetic fields. Under these experimental conditions, we obtained the extinction coefficient $\alpha(\lambda)$ of nanofluids (Figure 2) from transmittance spectra using the method described in [26, 27].

![Figure 2: Spectral extinction coefficient of goethite aqueous suspensions in the absence of external applied magnetic field.](image)

Then, we carried out magnetic-field-dependent transmittance measurements in the spectral range from the UV (300 nm) to the NIR (1500 nm). Nanofluids were held in quartz cuvettes of 2-mm path length and put in a specially designed non-magnetic holder, able to create magnetic fields of various directions and strengths by means of permanent magnets.

In Figure 3 we show some examples of transmittance spectra with no applied magnetic field and with a 5.6 mT magnetic field and different polarizations of the input beam (no polarization selection at the output). As a technical comment on Fig. 3, the spectral range of investigation is reduced with respect to that in Fig. 2 owing to the larger sample thickness required by this kind of measurement, arising in practically zero transmittance for wavelengths longer than 1400 nm.

![Figure 3: Polarized transmittance spectra of aqueous colloids in the absence of applied magnetic field (black curve B=0) and with 5.6 mT magnetic field at various polarizations. E, H, k indicate the](image)
electric and magnetic field and propagation vector, respectively, of the incoming electromagnetic wave (linear polarization), see also Fig. 1 for the notation.

From Figure 3 we can observe that goethite nanorods are oriented by the magnetic field. Consequently, the transmittance spectrum changes in a complex way. In can be useful, for fixed polarization, to consider the relative change in the spectral transmittance $T(\lambda,B)-T(\lambda,0)$ with and without applied magnetic field $B$ (Figure 4). A common characteristics we detected for all polarizations, is that the induced change monotonically depends on the strength of the external magnetic field. However, the obtained spectral dependence is different according to the considered polarization. It is possible to identify two main cases, i.e. a transmittance increase or decrease under the applied field. The transmittance increases with the applied field when the polarizations are (see the scheme in Figure 1 for reference): H parallel to B (i.e. E, k normal to B, i.e. with the external field oriented perpendicularly to both the beam propagation and the wave electric field) and both E & H normal to B (i.e. with the external magnetic field oriented along the beam propagation direction). On the other hand, the transmittance decreases when E is parallel to B (H, k normal to B). Moreover, we can observe that when the applied magnetic field is perpendicular to the beam propagation direction, the two polarizations $E||B$ and $H||B$ show different spectral characteristics, meaning that the sample becomes (magnetically induced) birefringent. On the other hand, when the external magnetic field is along the propagation direction of the beam, the two perpendicular polarizations (both $E,H_|_B$) show identical transmittance spectra, as expected, being the rods oriented with their main axis along the direction of the probe beam. In this case, the external magnetic field induced changes in the spectra with respect to the case with $B=0$ (Figure 4, b), but these changes are the same for the two polarizations (i.e. the sample is not birefringent).
Figure 4: Transmittance changes induced by an applied magnetic field of various strengths and directions.

For a quantitative evaluation, we can define, for fixed input polarization, the total extinction coefficient $\alpha_{\text{tot}}(\lambda, B)$ of the colloid in presence of the magnetic field B, as the sum of a component $\alpha(B=0)$, independent on the magnetic field and measured in the absence of the field itself (Figure 2), and a magnetic-field-dependent component $\Delta\alpha(\lambda, B)$:

$$\alpha_{\text{tot}}(\lambda, B) = \alpha(B = 0) + \Delta\alpha(\lambda, B) = \alpha_0 + \Delta\alpha \quad (1)$$

Under the hypotheses of negligible coherent effects and negligible multiple transmissions through the sample, the spectral transmittance $T(\lambda, B)$ can be simply expressed by the relationship:

$$T_B(\lambda, B) \propto \exp(-\alpha_{\text{tot}}(\lambda, B)) x \quad (2)$$

where $x$ is the sample thickness and the proportionality factor in Eq (2) takes into account the reflection losses at interfaces. If these losses can be kept constant, as in our sequential transmittance measurements where the cuvette is filled at the beginning, when $B=0$, and then remains untouched for all subsequent measurements, from the ratio between the experimental transmittances acquired at a given value $B$ ($T_B$) and at $B=0$ ($T_0$), we can obtain the field-dependent contribution $\Delta\alpha$ to the extinction coefficient as:

$$\ln \frac{T_B}{T_0} = -(\alpha_0 + \Delta\alpha)x + \alpha_0 x \quad (3)$$

thus:

$$\Delta\alpha = -\frac{1}{x} \ln \left( \frac{T_B}{T_0} \right) \quad (4)$$

Figure 5 shows the resulting extinction coefficient obtained from Eq. 4 for the three investigated polarizations. We can see that the extinction coefficient can be varied, even of a considerable extent under the application of an external magnetic field (e.g., for $B=5.6$ mT, about +16% for $E||B$, -26% for $H||B$ and -8% for $E,H\perp B$ at 500 nm and +33%, -29% and -8% at 600 nm for the three polarizations, respectively).
Figure 5. Total extinction coefficient of the aqueous colloid for the three polarizations and at different values of the external magnetic field. The plots have been restricted to the spectral range 470-1400 nm of the zero value of transmittance outside the considered interval, which prevents the use of Eq. 4 (see also Fig. 3).

To separate the spectral contribution given by nanoparticles from that of the surrounding fluid, we repeated the investigation of magnetic-field dependent transmittance, measuring the spectra against an identical cuvette filled with the base fluid only. The spectra where the bare fluid contribution was subtracted are shown in Figure 6 and agree with those obtained in the case of the nanofluidic system considered as a whole (Figure 4). Small discrepancies, which, however, are not larger than 3-4% below 1400 nm (Figure 7) can be ascribed to intrinsic experimental uncertainties of transmittance.
measurements. Differences above 1400 nm, where splitting curves of nanofluids go to zero, while those of nanoparticles are different from zero can be explained in terms of the known higher sensitivity of measurements against the base fluid, which are able to detect even very small signals on a similar background. Finally, we can notice from Fig. 8 than the splitting curves of nanoparticles are smoother than those of the nanofluid, which shows, instead, some spectral features in correspondence to the absorption peaks of the base fluid (water). Ruling out the simplest hypothesis of a non-complete compensation of the base fluid contribution due, for instance, to a slight tilt of the cell producing small differences in sample thickness among transmission measurements (in fact, in our protocol, the cell is put in its position at the beginning and never touched during the sequence of acquisitions), we could explain the appearance of water features in terms of the orientation and displacement of magnetic nanoparticles induced by the applied magnetic field. In fact, if nanoparticles move under the effect of the external field, the effective volume ratio of nanoparticles and base fluid on the sample volume crossed by the optical beam changes as well, allowing some water contributions to emerge, as curves in Figure 4 are obtained as simple differences of transmittances. The same phenomenon takes place during the measurements against the base fluid. However, in this case, the experimental transmittance curves are obtained as the ratio between nanofluid and water signals, so that these small motion effects are naturally hidden by the ratio procedure calculating the transmittances themselves.

Figure 6: Transmittance change induced by an applied magnetic field of various strengths and directions, nanoparticle contribution only.
Finally, the optical activity of the nanofluid under external applied magnetic field was qualitatively checked. We carried out transmittance measurements polarizing both the input and output beams and systematically acquiring the spectra with parallel and crossed polarizers, as a function of the applied magnetic field direction and strength. For fixed applied magnetic field and input beam polarization, we defined as the spectral rotation $\text{Rot}(\lambda)$ the difference in the spectral transmittances acquired with parallel ($||$) and crossed ($X$) polarizers, normalized to the average transmittance value:

$$\text{Rot}(\lambda) = \left( T_{||\text{polarizers}}(\lambda) - T_{X\text{polarizers}}(\lambda) \right) \left( \frac{T_{||\text{polarizers}}(\lambda) + T_{X\text{polarizers}}(\lambda)}{2} \right)^{-1}$$

From the experimental point of view, this measurement is affected by intrinsically low signal-to-noise ratio in the case with crossed polarizers. Therefore only a qualitative suggestion of the nanofluid behavior can be obtained. If the external magnetic field is directed along the beam propagation direction, the optical activity of the nanofluids seemed basically unchanged with respect to the case without applied field. On the other hand, if the applied magnetic field is perpendicular to the beam direction, the optical activity of the nanofluid is spectrally perturbed in different ways according to the polarization of the input probe beam (along the magnetic field direction or orthogonally to it). In any case, the perturbation increases with increasing magnetic field values (Figure 8).

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**Figure 7:** Comparison of obtained splittings in the cases of nanoparticles (continuous lines) and nanofluid as a whole (dotted lines) at $B=5.6$ mT.
The results of transmittance measurements carried out on samples suspended in PAO are shown in Figure 9. We can immediately notice a fundamental difference with respect to the previously shown aqueous suspensions: for PAO sample, the optical transmittance change did not show a monotonic dependence on the strength of the applied field. In fact, in this case, the sample show a transmittance change for the two lowest values of magnetic field (0.9 and 2.95 mT), while, if the field is further increased, no significant change was observed with respect to the 2.95 mT case. Even if temperature-dependent measurements would be needed to draw a conclusion, this result can be reasonably explained considering the significantly higher viscosity of PAO compared to water. The monotonic transmittance change observed for water-based suspensions comes from the progressively higher fraction of nanorods oriented increasing magnetic field strength. Conversely, Brownian motion tends to randomly re-orient the rods opposing to orientation to a specific direction. Brownian motion is of course less effective in PAO due to the higher viscosity and the saturation of optical transmittance change is achieved at lower magnetic field strengths. As for the induced birefringence, the results are the same as for the previous sample F1, with a magnetic-field induced birefringence for the E\|B, H\|B polarizations and no birefringence when the magnetic field is parallel to the optical beam propagation direction.
Finally, for a quantitative comparison of obtained results both for water and PAO suspensions, we calculated the integral of polarized transmittance curves as a function of the applied magnetic field (Figure 10). For the aqueous suspension F1 (Fig. 10a), the total transmittance monotonically depends on the applied magnetic field, either increasing (H||B and E,H||B polarizations) or decreasing (E||B polarization). As for the E||B and E,H||B polarizations, even if the effect of magnetic field is spectrally dissimilar (Figure 4) the integrated transmittance values can be nearly superimposed (Fig. 10a). This behavior is different from that shown by the PAO suspension F2, where the integrated transmittance differences for E||B and E||B polarizations are almost symmetrically located around the values obtained for the E,H||B polarization.

Figure 9: Transmittance change induced by an applied magnetic field of various strengths and directions for PAO-based colloids.
Conclusions

In this work, stable suspensions of goethite nanorods were successfully prepared in water and PAO. Optical properties as a function of an external magnetic field have been assessed as a function of the probe beam polarization and magnetic field direction and strength. The external magnetic field orients the goethite nanorods, producing a change in their transmittance spectrum for the different probe beam polarizations. Both the spectrally integrated values of transmittance and the wavelength-dependent values are modified by the external magnetic field, as well as the rotation of the polarization induced by the light propagation in the colloid. When goethite nanorods are suspended in water, the induced changes in the polarized spectral transmittance are a monotonic function of the magnetic field value, with a sign difference (transmittance increase or decrease with respect to the case with no applied field) related to the reciprocal directions of applied magnetic field and beam polarization. On the other hand, when magnetic nanoparticles are suspended in PAO, a saturation effect is shown on the magnetic-field induced changes of the spectral and integrated transmittance. The described results show that the optical properties of goethite-based suspensions are very sensitive to even weak external magnetic fields, with promising perspectives for sensing applications, also involving the incorporation of fluorescent dye, as well as for magnetically-driven smart materials, e.g. in display technology. Moreover, for water-based colloids, the spectral values of the magnetic field-dependent extinction coefficient is given.

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