Introduction

Magnetic nanoparticles (MNPs), mainly nanoparticles of iron oxides, like magnetite, have been widely used for immunological detection and the separation of targeted molecules, especially for biological and environmental samples. However, a spectrophotometric investigation of MNPs has not been extensively developed, though reports on the application of magneto-optical property of MNPs suspension can be found. Magneto-optical phenomena commonly include Faraday rotation, magnetic circular dichroism (MCD), magnetic linear dichroism (MLD) and magnetic linear birefringence. Recently, we have reported a simple relationship between the Faraday rotation angle and the concentration of lanthanide ions in aqueous solutions, and demonstrated the possibility of microscopic Faraday rotation imaging of micro-diamagnetic and paramagnetic samples. The use of MCD for the chiral recognition of 2-alkylalcohols with J-aggregates of the diprotonated porphyrin has also been reported. A reason why ordinary spectrophotometry was not applied to MNPs would be the fact that the absorption spectra of iron oxide MNPs do not show any characteristic maxima in UV-Vis region. In the present study, we discovered that iron oxides magnetic nanoparticles exhibit distinct magnetic orientational linear dichroism (MOLD) spectra having a maximum in the UV wavelength region, and that the MOLD spectra are sensitive to changes of the rotational motion or dispersion state, which is caused by viscosity changes of medium or the agglomeration of MNPs. The measurement method of MOLD spectra is the same as MLD spectra, which are obtained as the difference between the absorbances observed by a horizontally polarized light and a vertically polarized light. However, the origin of the phenomena is different between MOLD and MLD. Intrinsically, the MLD results from Zeeman splitting of the electronic states of orbitals, but MOLD is caused by the magnetic orientation of MNPs, as discussed in Ref. 13. Sometimes, MOLD is called as the Cotton-Mouton effect. We confirmed in the present study that the polymerization of the liquid medium including MNPs, which formed a resin film, and the agglomeration of MNPs by a chemical interaction with metal ions in aqueous solutions can greatly affect the MOLD spectra. The experimental results demonstrated that the MOLD spectra of MNPs have high potential as a sensitive probe of chemical/physical interactions of MNPs, which can be measured by simply applying a magnetic field by using a pair of permanent magnets in a sample compartment of a spectropolarimeter.

Experimental

Materials

Water-based MNPs, containing 10 nm magnetite in diameter (Taiho Kogyo, Ferricolloid, W-40, stabilized by the mixture of 8% oleic acid and 6% dodecylbenzenesulfonate), were used as the first MNPs sample. The concentration of magnetite in the original product was determined to be 36.6 wt% by a conventional spectrophotometry using complexation with 1,10-phenanthroline after dissolving the sample MNPs by adding proper volumes of 6 M HCl, reducing Fe(III) by 1.4 M HONH₂Cl, and buffering the acidic solution by 6.5 M CH₃COONH₄. As the second MNPs sample, COOH-modified MNPs dispersed in water was purchased from FerroTec (EMG707), which contained 16.5% magnetic nanoparticles with 10 nm in diameter. Reagent-grade FeCl₃·6H₂O was purchased from Wako and used dissolved in water. Water-based MNPs, containing 10 nm magnetite in diameter (Taiho Kogyo, Ferricolloid, W-40, stabilized by the mixture of 8% oleic acid and 6% dodecylbenzenesulfonate), were used as the first MNPs sample. The concentration of magnetite in the original product was determined to be 36.6 wt% by a conventional spectrophotometry using complexation with 1,10-phenanthroline after dissolving the sample MNPs by adding proper volumes of 6 M HCl, reducing Fe(III) by 1.4 M HONH₂Cl, and buffering the acidic solution by 6.5 M CH₃COONH₄. As the second MNPs sample, COOH-modified MNPs dispersed in water was purchased from FerroTec (EMG707), which contained 16.5% magnetic nanoparticles with 10 nm in diameter. Reagent-grade FeCl₃·6H₂O was purchased from Wako and used dissolved in water. Water was distilled and deionized by a Milli-Q system (Millipore, USA). UV curable resin (Toagosei, Biosurface AWP-MR (12%)) was used to prepare MNPs containing polymer film in the absence and presence of a magnetic field. Twenty microliters of the UV curable resin and 5 μL of the original W-40 dispersion were mixed on a glass slide with a
shallow dip, covered by a cover glass and irradiated by UV light (365 nm) for 1 h to make a hard polymer film under the presence of a magnetic field of 41 mT or in the absence of a magnetic field to make a control sample. The application of a higher magnetic field caused the migration of MNPs before hardening of the polymer, and gave a serious gradient in the concentration of MNPs in the polymer film.

Measurements of MOLD spectra

For measurements of suspension samples, 300 μL or 3 mL of aqueous dispersion of MNPs was put into a 1-mm or 10-mm quartz cell. A pair of permanent magnets of Nd-Fe-B was set to apply the magnetic field transversally to the light beam in the sample compartment of a Jasco J-820E spectropolarimeter. The permanent magnets were fixed on the rack & pinion stage, which could be manually moved for a distance of 50 mm each (Fig. 1A). By this method, a magnetic field of 0.4 – 190 mT was applied to the cell. The magnetic field at the position of a beam in the cell was measured by a Gauss meter (F. W. Bell, 5180) with a transverse Hall probe (F. W. Bell, STD18-0404). The MOLD spectra were measured with a LD mode of the spectropolarimeter in the range of 300 – 700 nm at a response time of 0.5 s with 0.5 nm resolution. For measurements of the polymer resin film, a glass slide having the polymer film was attached on a rotation mount (Thorlabs, RSP1/M) with a double-sided tape and the LD spectra were measured at every 10 degrees. All measurements were done in a thermostated room at 25 ± 1.5°C.

Results and Discussion

MOLD spectra in liquid and resin film

The MOLD spectra of MNPs dispersion in water were measured by changing the magnetic field. Typical magnetic field effects on the UV-Vis absorption spectra and the linear dichroism spectra of W-40 MNPs are shown in Fig. 1. The absorption spectra, which have no characteristic maxima, were not changed by the magnetic field (Fig. 1B), but the MOLD spectra increased with an increase of the magnetic field, exhibiting a maximum at 325 nm (Fig. 1C). The relationship between the maximum value of MOLD and the magnetic field showed a kind of saturation curve (Fig. 1D), which was well analyzed by the Langevin equation,

$$MOLD(B) = MOLD_{sat} L(x) = MOLD_{sat} \left( e^x + e^{-x} - \frac{1}{3} \right),$$

where

$$L(x) = \left( e^x - e^{-x} - \frac{1}{3} \right).$$

Here, $MOLD(B)$ is the MOLD value at a magnetic flux density $B$, $MOLD_{sat}$ is the saturated MOLD value in a sufficiently high magnetic field and $x$ is a variable, $x = \mu B k_B T$, which depends on the magnetic moment of MNP, $\mu$, the Boltzmann constant, $k_B$, and the absolute temperature, $T$. In a sufficiently low magnetic field, a simple linear relation between $MOLD(B)$ and $B$ is approximated by $MOLD = MOLD_{sat} \mu B / 3 k_B T$, and the slope of plots of $MOLD(B)$ vs. $B$ can be used to determine the magnetic moment parameter, $\mu / k_B T$. The saturated MOLD value is correlated to the apparent extinction coefficient, $\varepsilon$, of...
MOLD for the MNPs in a solution at a given wavelength by

$$MOLD_{sat} = \varepsilon ml,$$

(2)

where $m$ is the concentration of MNPs (wt%) and $l$ is the optical path length of the cell (cm). Then, the observed MOLD spectral change will be characterized by using the two apparent parameters of $MOLD_{max}$ and $\mu/k_B T$.

For the case shown in Fig. 1, the parameters of $MOLD_{max} = 0.024$ and $\mu/k_B T = 50.0 (1/T)$ were obtained from the fitted curve shown in Fig. 1(D). From the two observed parameters, the magnetic moment of $\mu = 2.05 \times 10^{-19}$ JT$^{-1}$ was calculated, which corresponds to $2 \times 10^4$ of magneton. For another sample of EMG707, we could obtain $\mu = 7.16 \times 10^{-19}$ JT$^{-1}$.

When the concentration of MNPs (W-40) was changed over a wide range of $10^{-5} - 10^{-1}$ wt%, the value of MOLD under 188 mT was linearly proportional to the concentration, as shown in Fig. 2. The linear relationship confirmed that the MOLD values are due to the magnetic orientation of single MNPs, and that there is no remarkable agglomeration of the MNPs which might affect on the magnetic orientation of MNP. From the intercept of the linear plot, the apparent extinction coefficient was calculated as $\varepsilon = 25.9$ (wt%)$^{-1}$ cm$^{-1}$ at 324.5 nm.

The results of Fig. 1 and Fig. 2 strongly suggested that the optical transition moment of MNP is parallel to the easy axis of the magnetization of MNPs. To confirm this point, UV curable resin films containing MNPs was prepared under no magnetic field and a magnetic field. At first, the film prepared under no magnetic field was measured, but it had no MOLD spectra, indicating that the MNPs particles are randomly oriented and rotationally fixed in the film. Next, the film prepared under a magnetic field of 41 mT was set on a rotation mount, as shown in Fig. 3(A) and LD spectra were measured rotated every 10 degrees. The LD spectra changed depending on the rotational angle, $\theta$, (Fig. 3(B)) and the change of the LD values at 330 nm were fitted by the correlation function $\cos^2 \theta$ (Fig. 3(C)), which is known as Malus’s law on the intensity of a polarized light passing through a polarizer. Then, it was proved that the easy axis of the magnetization of MNPs is parallel to the MOLD transition moment of MNPs.

Detection of agglomeration by MOLD spectra

When Fe(III) ion was added to the COOH modified MNPs (0.0165%) aqueous dispersion in a 1-mm cell under a constant magnetic field of 29 mT, the maximum wavelength of the MOLD spectra shifted from 330 nm to a longer wavelength (Fig. 4(A)) and the maximum value in the MOLD spectra decreased (Fig. 4(B)) with an increase of the Fe(III) concentration, suggesting agglomeration of the MNPs. At an iron concentration of $1.93 \times 10^{-4}$ M, the maximum MOLD wavelength shifted to 389 nm and the maximum value of the MOLD decreased to a minimum value of 0.0037, as shown in Fig. 2. The linear relationship confirmed that the MOLD values are due to the magnetic orientation of single MNPs, and that there is no remarkable agglomeration of the MNPs which might affect on the magnetic orientation of MNP.
Fe³⁺ on the surface of the MNPs. The correlation between the deagglomeration due to the excess adsorption of the cationic iron(III) ion, and a further addition of iron(III) ion induced agglomeration of the MNPs occurred at a specific concentration. COOH modified MNPs reacted with iron(III) ion and the shown in Figs. 4(A) and (B). The results suggested that the S mold wavelength, shifted to a lower iron(III) concentration, as the resin formation of the media and the metal ion-induced agglomeration of MNPs. Further applications of MOLD spectra to the critical detection of weak interactions between MNPs and chemical additives are continuing.

Figs. 4(A) and 4(B). In this situation, fine agglomerates were thought to be formed. In the higher concentrations of iron(III), the maximum wavelength and the maximum MOLD value tended to return to the initial value before the agglomeration. When the initial concentration of MNPs was lower, the iron(III) concentration, showing the minimum MOLD and the maximum wavelength of MOLD spectra in the four different MNPs (EMG707). The results suggested that the COOH modified MNPs reacted with iron(III) ion and the agglomeration of the MNPs occurred at a specific concentration of iron(III) ion, and a further addition of iron(III) ion induced deagglomeration due to the excess adsorption of the cationic Fe³⁺ on the surface of the MNPs. The correlation between the specific iron(III) concentration and the initial MNPs concentration is shown in Fig. 4(C), which gives a linear plot in the logarithmic scale with a proportional coefficient of 1.48 and an intercept of 3.73, that is, [MNPswt%] = 5339 [Fe³⁺]⁻¹. This means that the required concentration of iron(III) to agglomerate 1 wt% of the MNPs is [Fe³⁺] = 3.03 × 10⁻³ M.

Interestingly, the maximum wavelength of the MOLD spectra was also sensitive to the agglomeration, showing a large red shift from 330 to 387 nm at a specific iron(III) concentration, and then back to 340 nm at the higher iron(III) concentration, in which deagglomeration occurred. The large red-shift of the maximum MOLD wavelength of MNPs caused by the agglomeration is thought to suggest electrostatic stabilization of the Fe³⁺-Fe²⁺ charge migration in the magnetite nanoparticles, though the spectroscopic study of MNPs is still limited. In conclusion, it was demonstrated that the MOLD spectra of MNPs are useful to sense the rotational motion of MNPs, which can be affected by various gentle interactions, such as the resin formation of the media and the metal ion-induced agglomeration of MNPs. Further applications of MOLD spectra to the critical detection of weak interactions between MNPs and chemical additives are continuing.

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