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果報告書 (自然科学分野)

ピッカリングエマルションを構成する磁性ナノ粒子の交流磁場下

配向ダイナミクスの研究

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Introduction

Magnetic nanoparticles (MNP) have been widely used in the biomedical field, specifically in drug delivery, enzyme immobilization, and many other applications. In order to find a less toxic solvent system for applying cosmetics or other bio-applications, Pickering emulsion is a good alternative and came to be a replacement for hazardous materials. Pickering emulsion usually arises from solid particles on the interface of two immiscible solvent systems, such as oil and water [1]. Although some publications studied the macro-phenomenon[2] and synthesis methodologies[3], the micro-environment observation has not been conducted yet. Recently, Prof. Tsukahara and Dr. Suwa gave meaningful insight into the MNP's motion in the toluene or water [4, 5]. We want to extend the measurement of the interfacial motion from single phase to mix phase, and this will be a fundamental study in colloid and interface science. This proposal will focus on orientation behavior in magnetic Pickering emulsion, and this observation at the interface will give valuable insight correlated to the local viscoelasticity.

Methods

Synthesis of iron oxide nanoparticle

Coprecipitation method was used to synthesize a bare iron oxide nanoparticle. Briefly, $FeCl_3 \cdot 6H_2O$ and $FeCl_2 \cdot 4H_2O$ were dissolved in water ($Fe^{3+}:Fe^{2+} = 2:1$). The solution was bubbled with nitrogen gas for 5 min and then heated the solution to 70 °C. NH₄OH_{aq} was dropped into the solution, black precipitate occurred. The mixture was heated to 80 °C for 30 min. The resulted black particle was separated with a permanent magnet and washed with water and ethanol. Finally, magnetic material was dried with a vacuum until use.

Modification of iron oxide nanoparticle

The synthesis procedure followed according reference [6] with slight modification. For surface functionalization purposes, 5 mL of 20,000 mg L⁻¹ poly(sodium 4-styrenesulfonate) (PSS) solution mixed directly with 5 mL of 80,000 mg L⁻¹ bare iron oxide and then diluted with 10 mL of deionized water. The suspension of Fe₃O₄@PSS was mixed with homogenizer (T50 homogenizer, IKA, Germany) at 500 rpm for 24h. After surface modification, Fe₃O₄@PSS solution was washed with deionized water twice for removal the unreacted PSS molecule. For further modification with cationic surfactant, 10 mM CTAB solution was prepared first and further mixed Fe₃O₄@PSS solution with high speed homogenizer (AHG-160D, AS

ONE, Japan) which installed a shaft generator (HT-1008, AS ONE, Japan) at 10000 rpm for 5 min.

Synthesis of magnetic Pickering emulsion (MPE)

5 mL Fe₃O₄@PSS@CTAB and 5 mL dodecane was synthesized with a high-speed homogenizer (AHG-160D, AS ONE, Japan) at 10,000 rpm for 5 min. The product was a 10 mL magnetically responsive oil-in-water emulsion composed of 5,000 mg/L of IONPs-PSS and 5 mM excess CTAB.

Magnetic linear birefringence (MLB) measurement

The orientational behavior of MNP can be measured with magnetic linear dichroism (MLD) induced in the MNP suspension because MLD has a linear relation with $\langle \cos^2 \theta \rangle$, where the angle bracket indicates the ensemble average and θ is the angle between the optic axis of MNP and the field. The apparatus, which has been constructed in Prof. Tsukahara's Lab[4], measures the MLD in an alternating magnetic field, whose frequency range is from 0.3 Hz to 40 kHz and amplitude is up to 45 mT. The orientational behavior will be revealed by the analysis of the frequency dependence of the MLD signal.

However, since MPE exhibited high optical extinction at 405 nm such that the MLD could not be measured, we changed the configuration of the setup to measure the magnetic linear birefringence (MLB) with near-infrared light (785 nm) The apparatus for MLB measurement is shown in **Fig. 1**. The diode laser of 785 nm in wavelength was used for incident light. The light was polarized to 45° with respect to the field. The transmitted light was elliptically polarized, the ellipticity of which was equal to the half of the retardation, $\Delta/2$. A quarter wavelength plate (QWP) converted the elliptic to the linear polarized light, whose the polarized angle tilted $\Delta/2$ from the original polarizing plane. A Wollaston prism separate the transmitted light into two beams polarizing parallel and perpendicular to the field. We estimated the MLB, that is Δ , from the difference in the intensity of these two beams. When the same MNP suspension was measured, MLB was proportional to MLD. Therefore, the MLB also has linear relation with $<\cos^2\theta$.

The dominant frequency of MLB was 2f, where f is the field frequency. A lock-in amplifier allowed us to precisely measure the amplitude and the phase of 2f component of MLB. The signal was separated into real (in-phase) and imaginary (quadrature) parts to represent the rotational dynamics of MNPs.



Fig. 1 The schematic diagram of magnetic linear birefringence instrument.

Results and discussion

MLB measurement of surface modification on iron oxide nanoparticle

The spectra of MLB measurement can represent with two different profile, real part and imaginary part. From the observation of **Fig. 2**, bare iron oxide nanoparticle and Fe₃O₄@PSS showed similar profile. However, Fe₃O₄@PSS@CTAB showed different pattern of real and imaginary part. This phenomenon indicated that rotation motion of magnetic particle changed by the long alkyl chain from CTAB surfactant.



Fig.2 Frequency spectra of the 2f component of MLB (MLB₂) of magnetite MNPs with different surface modifications.

MLB measurement of different viscosity of Fe₃O₄@PSS solution

Viscosity is an important parameter in the behavior of MLB measurement. The

viscosity was adjusted by glycerol concentration in Fe₃O₄@PSS suspension. The imaginary peak shifted to a lower frequency with the increase in viscosity. We further estimated the parameters such as A_0 (initial MLB value), τ_0 (relaxation time), and β (exponent parameter which will influence peak shape) with two types of non-linear fitting by the Cole-Cole equation (1, referred to as "simple fit") [7] and the square of the Cole-Cole equation (2, referred to as "complex fit").

$$\operatorname{Im}[MLB] = \frac{A_0(\omega\tau_0)^\beta \cos(\frac{\pi(1-\beta)}{2})}{1+2(\omega\tau_0)^\beta \sin(\frac{\pi(1-\beta)}{2}) + (\omega\tau_0)^{2\beta}} (1), \text{ where } \omega = 4\pi f$$
$$\operatorname{Im}[MLB] = \frac{A_0 \sin(2 \operatorname{atan}(\frac{(\omega\tau_0)^\beta \cos(\frac{\pi(1-\beta)}{2})}{1+(\omega\tau_0)^\beta \sin(\frac{\pi(1-\beta)}{2})})}{1+2(\omega\tau_0)^\beta \sin(\frac{\pi(1-\beta)}{2}) + (\omega\tau_0)^{2\beta}} (2), \text{ where } \omega = 4\pi f$$

The Cole-Cole equation is a suitable relaxation model when the relaxation time has distribution. It was reported that under an alternating magnetic field, MNPs with small anisotropy energy, such as smaller iron oxide nanoparticles, physically oscillated at 2f keeping alignment to some extent [2, 3], and the simple fit (eq.1) seems appropriate model. On the other hand, the complex one (eq. 2) assumes that the direction of the MNP's easy axis reverses with the field. We can find the correlation coefficients showed simple fit was better than complex fit. Relaxation time (τ_0) was found that have a reverse linear relationship with viscosity (**Fig. 5**).



Fig.3 MLB measurements of different viscosity Fe₃O₄@PSS solution. The viscosity was changed with different weight percent of glycerol addition.



Fig.4 Nonlinear fitting of different viscosity Fe₃O₄@PSS solution. (a) 0 wt% glycerol (b) 10 wt% glycerol (c) 20 wt% glycerol (d) 30 wt% glycerol of Fe₃O₄@PSS solution.

Complex fit	ε ₀	$ au_0$	β	r ²	Viscosity	VH (cal.)	VH (DLS)
		(ms)			(Pa s)	(nm)	(nm)
0 wt%	6.07E-03	2.09E-04	8.01E-01	9.89E-01	8.90E-04	68.56	168.7
10 wt%	5.88E-03	1.31E-04	8.01E-01	9.89E-01	1.05E-03	55.43	
20 wt%	5.79E-03	1.74E-04	7.97E-01	9.90E-01	1.58E-03	53.20	
30 wt%	6.23E-03	2.34E-04	8.03E-01	9.90E-01	2.20E-03	52.62	
Simple fit	ε ₀	$ au_0$	β	r ²	Viscosity	VH (cal.)	VH (DLS)
Simple fit	ε ₀	τ ₀ (ms)	β	r ²	Viscosity (Pa s)	VH (cal.) (nm)	VH (DLS) (nm)
Simple fit	ε ₀ 6.07E-03	τ ₀ (ms) 2.69E-04	β 9.51E-01	r ² 9.96E-01	Viscosity (Pa s) 8.90E-04	VH (cal.) (nm) 74.55	VH (DLS) (nm) 168.7
Simple fit 0 wt% 10 wt%	ε ₀ 6.07E-03 5.92E-03	τ ₀ (ms) 2.69E-04 3.37E-04	β 9.51E-01 9.52E-02	r ² 9.96E-01 9.97E-01	Viscosity (Pa s) 8.90E-04 1.05E-03	VH (cal.) (nm) 74.55 75.97	VH (DLS) (nm) 168.7
Simple fit 0 wt% 10 wt% 20 wt%	ε ₀ 6.07E-03 5.92E-03 5.83E-03	τ ₀ (ms) 2.69E-04 3.37E-04 4.50E-04	β 9.51E-01 9.52E-02 9.48E-01	r ² 9.96E-01 9.97E-01 9.97E-01	Viscosity (Pa s) 8.90E-04 1.05E-03 1.58E-03	VH (cal.) (nm) 74.55 75.97 73.05	VH (DLS) (nm) 168.7

Table 1 Fitting results of different viscosity of Fe₃O₄@PSS solution.



Fig.5 Linear fitting between different viscosity and relaxation time of Fe₃O₄@PSS solution.

MLB measurement of different dilution buffer of Fe₃O₄@PSS solution

It was reported that the pH environment changed the surface charge of

Fe₃O₄@PSS. We changed pH in the range from 3 to 11. To adjust the sample to the proper concentration for MLB measurement, phosphate buffer was used for dilution. However, the MLB profile fluctuated when diluted with 10 mM phosphate buffer. This phenomenon may be due to the formation of Fe₃O₄@PSS aggregation in a solution with high ionic strength. The different ionic strength of phosphate buffer was examined. **Fig. 6** showed that the MLB frequency spectra changed when ionic strength exceeded 5 mM. Accordingly, 0.5 mM phosphate buffer was chosen as the dilution medium for further experiments.

Fig.7 shows the dependence of the MLB frequency spectra on pH, indicating that the imaginary peak shifted slightly to a lower frequency under pH 3. The reason can be explained with higher hydrodynamic diameter due to the protonation of PSS functionality, sulfonic group, which was protonated in an acidic condition.



Fig.6 MLB measurements of different dilution buffer of Fe₃O₄@PSS solution.



Fig. 7 MLB measurements of different pH environment of Fe₃O₄@PSS solution. 0.5 mM phosphate buffer was used for dilution magnetic solution.

MLB measurement of Magnetic Pickering Emulsion solution

In order to observe interfacial rotational dynamics, Magnetic Pickering Emulsion (MPE) was observed by MLB system. **Fig. 8** showed irregular profile in different batch of MPE measurement. These results might be attribute to two phenomenon, intrinsic scattering of droplet from laser irradiation and bad reproducibility of MPE formation.



Fig. 8 MLB measurements of Magnetic Pickering Emulsion. Original MPE was dilution 20 times with deionized water.

Conclusion

In this work, we examined the MLB profile with different modifications of iron oxide nanoparticles under aqueous conditions. Experimental results showed that the functionality of magnetic nanoparticles and viscosity would change the orientation behavior. Unfortunately, the profiles of MLB were not stable under MLB measurement because of the intrinsic scattering of numerous droplets in MPE solution under laser irradiation. It is interesting and worthy to investigate further in the future.

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