



Magnetophoretic velocity of microorganic droplets adsorbed by dysprosium(III) laurate in water

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Abstract

By using an improved apparatus for the observation of magnetophoresis, the magnetophoretic velocity of 2-fluorotoluene droplets including lauric acid was measured in aqueous dysprosium(III) solution. The magnetophoretic velocity of pure 2-fluorotoluene droplets was proportional to the square of the radius. On the other hand, the velocity of the organic droplets including lauric acid in the dysprosium(III) solution showed a deviation from the square radius relationship, more remarkably in smaller droplets than 2 μm in radius. These results indicated that the dysprosium(III)–laurate complex was formed at the liquid–liquid interface. This study is the first report on the detection of the interfacial complex by the magnetophoresis of the microdroplet.

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1. Introduction

Development of new techniques for the separation and characterization of microparticles has been extensively required in colloidal chemistry, environmental chemistry and biological sciences [1,2]. Field flow fractionation (FFF) [3] and split-flow thin fractionation (SPLITT) [4] have been developed for this purpose. These methods could separate particles in liquid by using external fields. However, they could not analyze the properties of individual particles.

Recently, a high magnetic field of 10 T has become available in laboratories due to the development of superconducting magnet, and some new applications of high magnetic field and some new findings have been reported. Beaugnon and Tournier

demonstrated magnetic levitation of diamagnetic materials [5], Ikezoe et al. performed the levitation of paramagnetic aqueous solution [6], and Yamato et al. succeeded in fabricating large-size polymer spheres by using magnetic levitation [7]. Application of high magnetic fields for separation was also reported. The paramagnetic metal ion could be separated from diamagnetic ion by a combination with thin-layer chromatography [8]. These methods utilize a magnetic force that depends on not only high magnetic field but also the gradient.

Magnetophoretic velocimetry is a new detection technique to measure the magnetic susceptibility and the composition of individual microparticles using a magnetic force [9]. In this technique, the size and the migration velocity of a microparticle are directly measured with a microscope and from their values the magnetic susceptibility can be calculated. By using the magnetic field (10 T) generated with a superconducting magnet, this technique allowed us

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to measure a volume magnetic susceptibility at the 10^{-6} level for a single microparticle [10].

The purpose of this study is to investigate whether the influence of paramagnetic species adsorbed at the interface of microdroplet is detectable by the magnetophoretic velocimetry. In this paper, the measurement apparatus of the magnetophoresis has been improved, so as to diminish some fluctuation in velocity from the flow of the medium and to increase the accuracy of the velocity measurement. Using the improved apparatus, the influence of the formation of the dysprosium(III)–lauric acid complex at the interface of a droplet on the magnetophoretic velocity was investigated from the droplet size dependency of the velocity.

2. Experimental

2.1. Chemicals

Lauric acid was purchased from Sigma (St. Louis, MO, USA). It was dissolved in 2-fluorotoluene to make a solution of $1.0 \cdot 10^{-2}$ M concentration. The stock aqueous solution of dysprosium(III) was prepared by dissolving dysprosium oxide (Dy_2O_3 , 99.9%, Nacalai Tesque, Kyoto, Japan) in $1.0 \cdot 10^{-2}$ M sulfuric acid. The stock solution was diluted to $[\text{Dy(III)}]=5.0 \cdot 10^{-4}$ M to be used for the measurement. The pH and the ionic strength of the Dy(III) aqueous solution were adjusted to 6.8 and 0.6 M, respectively, with 2-(*N*-morpholino)ethanesulfonic acid (MES) (Dojindo, DOTITE Good's buffer, Kumamoto, Japan) and sodium sulfate. The aqueous solution was saturated with 2-fluorotoluene prior to use to prevent a dissolution of 2-fluorotoluene droplets.

A 10- μl portion of the organic solution of lauric acid ($1.0 \cdot 10^{-2}$ M) was added to a 3-ml portion of Dy(III) aqueous solution of $5.0 \cdot 10^{-4}$ M, and then the mixture was sonicated for 1 min in water bath in order to disperse the organic phase to micrometer sized droplets in the aqueous solution.

Water was purified by a Milli-Q system (Millipore, Billerica, MA, USA) and the other reagents were used as received.

2.2. Apparatus

A high magnetic field of 10 T was generated by a cryogen-free superconducting magnet (JMT, JMTD-10T100HH1, Tokyo, Japan). The experimental setup used in this study was similar to the one described previously [10] and shown in Fig. 1a, but the sample introduction system was improved as shown in Fig. 1b. A sample solution was raised spontaneously into the square capillary cell (Polymicro Technologies, Phoenix, AZ, USA) by capillary phenomenon soon after the introduction of the sample into the reservoir. The capillary rise of the solution into the capillary stopped within 10 s after the introduction of the solution, and then the behavior of organic droplets in the aqueous solution near the edge of the pole pieces was observed by an objective (Mitsutoyo, Mplan Apo SL 20, Kanagawa, Japan), a tube lens (Mitsutoyo, MT-1, Kanagawa, Japan), and a charge-coupled device (CCD) camera (ELMO, ME421, Nagoya, Japan). The CCD image was displayed on a monitor and also recorded on video cassettes. The migration velocity and size of the droplet were measured from the images captured in a computer. After finishing an experiment, the sample solution in the capillary was discarded and rinsed using a vacuum pump.

All measurements were carried out in a thermostated room at 25 ± 1 °C.

3. Results and discussion

3.1. Magnetophoretic velocity of the organic droplets

Fig. 2 shows the magnetophoretic behavior of a single pure 2-fluorotoluene droplet in water. This image was made by superimposing microphotographs captured at 0.2 s intervals. We defined the direction of capillary cell as the *x*-direction and the edge of the pole pieces as $x=0$. The dashed line in Fig. 2 indicates $x=0$. The droplet was attracted to the gap of the pole pieces, and the migration velocity was maximized near the edge of the pole pieces. In Fig. 3, the *x*-components of magnetophoretic ve-

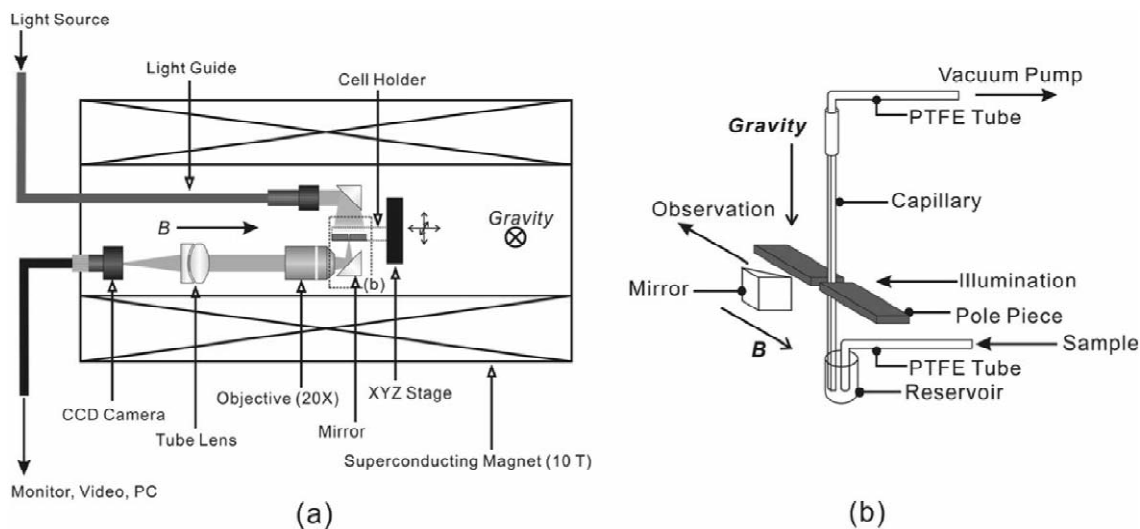


Fig. 1. Experimental setup for the measurement of the magnetophoretic velocity of microdroplet. (a) The schematic drawing of the overall apparatus. (b) Sample introduction system into the cell. The square capillary cell had an inner section of $100 \times 100 \mu\text{m}$ and outer section of $300 \times 300 \mu\text{m}$. The sample solution was raised into the cell by a capillary phenomenon soon after it was introduced into the reservoir. The rising flow stopped within 10 s after introduction, and then the magnetophoretic behavior of oil droplets dispersed in aqueous medium was observed.

locity of the organic droplet in Fig. 2 was plotted against x . The velocity had a maximum value at $x=30 \mu\text{m}$.

An x -component of the migration velocity, v_x (m s^{-1}), of a droplet under an inhomogeneous magnetic field, B (T), can be written as follows [9,11,12]:

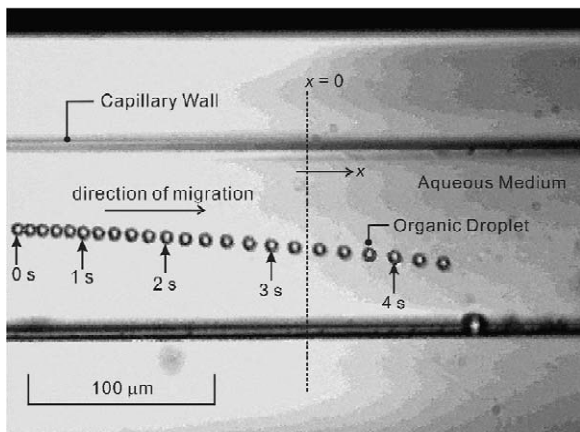


Fig. 2. The magnetophoretic behavior of a single microdroplet. This microphotograph was made by superimposing the images captured at 0.2 s intervals. The dashed line indicates the position of the edge of pole pieces ($x=0$).

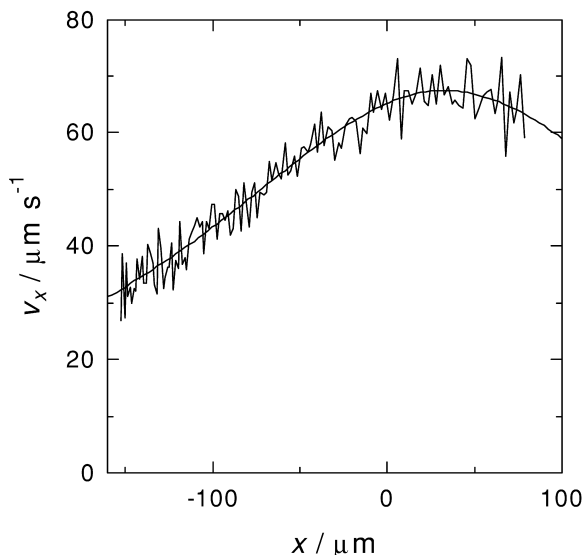


Fig. 3. Magnetophoretic velocity change of a single particle shown in Fig. 2. The solid line was fitting curve of Lorentzian, $v_x = v_{\text{max}}/[1 + (x - x_0)^2/w^2]$, where $v_{\text{max}} = 67 \mu\text{m s}^{-1}$, $x_0 = 33 \mu\text{m}$ and $w = 180 \mu\text{m}$.

$$v_x = \frac{2}{9} \cdot \frac{(\chi_p - \chi_m)}{\mu_0 \eta} \cdot r^2 B \cdot \frac{dB}{dx} \quad (1)$$

where χ_p and χ_m are the volume magnetic susceptibilities of a droplet and a medium (dimensionless, S.I. unit), respectively, μ_0 the vacuum magnetic permeability ($\text{T}^2 \text{J}^{-1} \text{m}^3$) and η a viscosity of medium (Pa s). A magnetophoretic velocity is directly proportional to the difference of magnetic susceptibilities between a droplet and a medium ($\chi_p - \chi_m$), a square radius, r^2 , and the product of a magnetic field and its gradient, $B(\text{dB}/\text{dx})$. In the system of a pure 2-fluorotoluene in water, ($\chi_p - \chi_m$) was equal to $0.82 \cdot 10^{-6}$. The value of $B(\text{dB}/\text{dx})$ as a function of x was calculated from the magnetophoretic velocity of polystyrene microparticle (4.6 μm in radius) observed in a 0.05 M manganese(II) chloride aqueous solution (the maximum value of $4.7 \cdot 10^4 \text{ T}^2 \text{m}^{-1}$) [6]. Taking into account of the values for ($\chi_p - \chi_m$) and $B(\text{dB}/\text{dx})$, the velocity profile of the droplet in Fig. 3 was found to be reasonable.

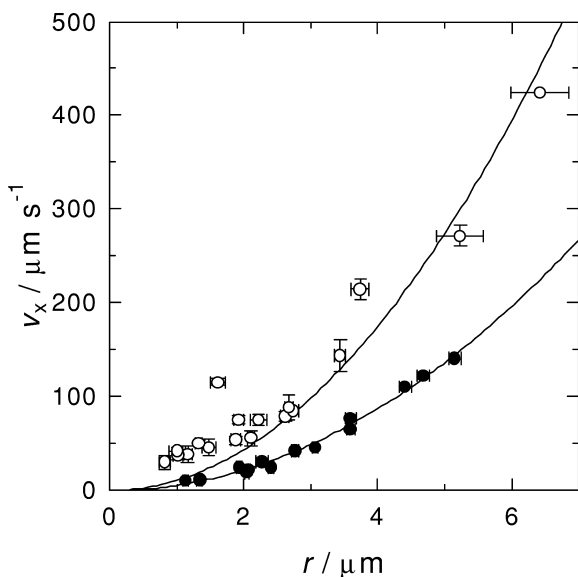


Fig. 4. The magnetophoretic velocity at $x=0$ plotted versus the radius of a droplet. The filled circles represents velocities in the absence of dysprosium(III) and lauric acid and the open circles in the presence of them. The lines were obtained by a least-square method of $v_x = ar^2$, where a is a constant.

Fig. 4 shows the plots of the magnetophoretic velocity of individual droplets of various sizes at $x=0$, where $B(\text{dB}/\text{dx})$ is equal to $4.0 \cdot 10^4 \text{ T}^2 \text{m}^{-1}$. The filled circles are the velocities of organic droplets in the absence of Dy(III) and lauric acid (pure 2-fluorotoluene droplets were dispersed in pH 6.8 aqueous solution whose ionic strength was 0.6 M). The open circles are those of the organic droplets which is containing $1 \cdot 10^{-2} \text{ M}$ lauric acid and dispersed in $5.0 \cdot 10^{-4} \text{ M}$ Dy(III) aqueous solution. The fitting curves were obtained by a least-square method with the equation of $v_x = ar^2$, where a is a constant. In both plots, the magnetophoretic velocities were almost proportional to the square radius as predicted in Eq. (1). In order to obtain the magnetic susceptibility of a droplet, the magnetophoretic velocity was divided by the square of the radius. Fig. 5 shows the normalized velocity, v_x/r^2 , as a function of radius. The symbols are the same meaning as in Fig. 4. Although Eq. (1) predicted that the normalized velocity was constant value of $5.6 \pm 1.0 \mu\text{m}^{-1} \text{s}^{-1}$, a significant reciprocal dependency on the radius was appeared in the presence of Dy(III) and lauric acid (open circles in Fig. 5).

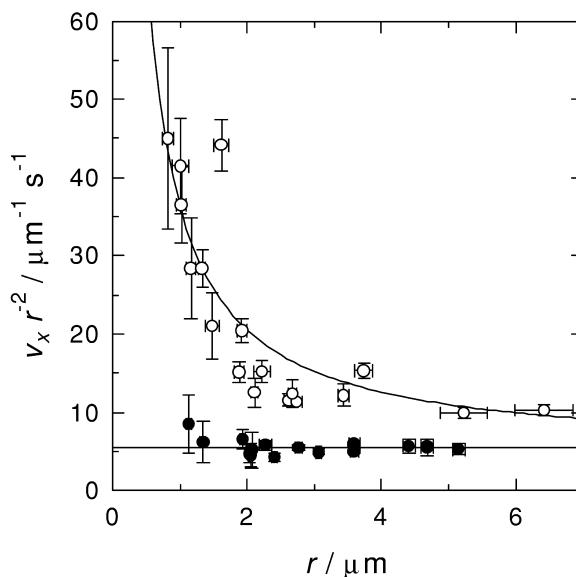


Fig. 5. The normalized magnetophoretic velocity as a function of radius. The open and filled circles are the same meaning in Fig. 2. The line for the open circles was the fitting curve with Eq. (3).

3.2. Influence of adsorption of dysprosium(III) on the droplet–medium interface

Adsorption of Dy(III) at the droplet–medium interface was considered to analyze the dependency of the normalized magnetophoretic velocity on the radius. It was confirmed by a batch method that the extraction of Dy(III) with laurate did not occur in this system. In addition, without either Dy(III) in aqueous medium or lauric acid in 2-fluorotoluene droplet, the normalized magnetophoretic velocity was independent of the radius and gave the same value as shown by filled circles in Fig. 5. The high stability constant of $8.7 \cdot 10^2 \text{ M}^{-1}$ for the 1:1 complex of hexanoic acid with dysprosium(III) was reported [13]. Furthermore, lauric acid should be adsorbed at the interface because it has a property of surfactant. The saturated interfacial concentration of $6.56 \cdot 10^{-10} \text{ mol cm}^{-2}$ at an air–water interface was also reported [14]. These facts suggest that the adsorption of dysprosium(III)–laurate at the 2-fluorotoluene–water interface is responsible to the radius dependency of the normalized magnetophoretic velocity.

The contribution of the adsorbed Dy(III) species to the magnetophoretic velocity can be discussed as follows. By using an interfacial concentration of dysprosium(III), C_{int} (mol m^{-2}), the amount of dysprosium(III) ions in the interface of a droplet can be expressed as $4\pi r^2 C_{\text{int}}$. Then, the magnetic susceptibility of the droplet can be written as follows:

$$\chi_p = 3\chi_{\text{Dy}}^{\text{M}} C_{\text{int}} / r + \chi_{2\text{FT}}^{\text{V}} \quad (2)$$

where the superscripts M and V refer to a molar and volume magnetic susceptibility ($\text{m}^3 \text{ mol}^{-1}$), respectively, and the subscripts Dy and 2FT indicate dysprosium(III) and 2-fluorotoluene, respectively. In this equation, the adsorbed Dy(III) ions are dealt as if they are homogeneously dissolved in the organic droplet. The contribution of lauric acid to χ_p could be neglected, because the diamagnetic molar susceptibility is small. Substitution of Eq. (2) into Eq. (1) yields the following equation expressing the normalized magnetophoretic velocity:

$$\frac{v_x}{r^2} = \frac{2}{9} \cdot \frac{[(3\chi_{\text{Dy}}^{\text{M}} C_{\text{int}} / r + \chi_{2\text{FT}}^{\text{V}}) - \chi_{\text{m}}]}{\mu_0 \eta} \cdot B \cdot \frac{dB}{dx} \quad (3)$$

The term of the reciprocal radius remains in Eq. (3). Using the reference value of the molar magnetic susceptibility of dysprosium(III) of $5.65 \cdot 10^{-7} \text{ m}^3 \text{ mol}^{-1}$ [15], the interfacial concentration of Dy(III), C_{int} , was estimated as $2.6 \cdot 10^{-10} \text{ mol cm}^{-2}$. This value seems reasonable, since it is comparable with the saturated interfacial concentration of lauric acid at an air–water interface. Therefore, the experimental results in Fig. 5, which showed a reciprocal tendency for radii, suggested a significant contribution of the adsorbing species of dysprosium(III) to the magnetophoretic velocity. To analyze more quantitatively this effect, the coordination number of laurate and the interfacial adsorption equilibria of Dy(III)–laurate should be considered.

In the present study, it was demonstrated that the interfacial adsorption of paramagnetic species at the surface of the droplet could be detected by the magnetophoretic velocimetry. The magnetophoretic velocity was changed by the interfacial adsorption of Dy(III)–lauric acid complex. The present results suggest that the adsorbed microparticles by a paramagnetic label compound can be separated selectively by magnetophoresis using the difference in the velocity. Magnetophoretic velocimetry could be utilized not only for the determination of the paramagnetic species in the bulk of a droplet but also at the liquid–liquid interface of the droplet, which has received a great deal of attention in various fields of chemistry and chemical technology [16,17].

Acknowledgements

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