

Electromagnetophoretic Migration Velocity of Organic Microdroplets with Surfactants Using Permanent Magnets

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By using the electromagnetophoretic migration technique with permanent magnets, the electromagnetophoretic migration velocimetry in a droplet-based system was demonstrated for organic droplets dispersed in an aqueous solution. Migration of 2-fluorotoluene droplets with a diameter of 8 – 16 μm dispersed in 1.0 M KCl aqueous solution could be achieved in the same manner as for solid particles. The effect of cetyltrimethylammonium bromide (CTAB) on the electromagnetophoretic migration velocity of the droplets was also investigated. When the concentration of CTAB was in the range from 10^{-6} to 10^{-4} M, the electromagnetophoretic migration velocity of 2-fluorotoluene droplets decreased as the concentration of CTAB increased. With this measurement, we could successfully characterize organic droplets in terms of the amount of adsorbing surfactants by evaluating the surface conductivity of organic droplets calculated based on their electromagnetophoretic migration velocity.

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Introduction

Droplet-based microfluidic systems have been drawing increasing attention as an attractive technique for high throughput and highly sensitive screening of small amounts of chemical and biological samples, owing to their suitability for handling the small size and limited volume of droplets.^{1–5} For such droplet-based systems, various analytical techniques such as fluorescence,^{6,7} electrochemistry,⁸ capillary electrophoresis,^{9,10} and mass spectrometry,¹¹ have been successfully applied to measure the chemical compositions of droplets. In addition to the method of analysis, the method of manipulating droplets is also important for controlling the reaction in or on the droplets.

Electromagnetophoresis is the migration phenomenon of micro-particles when an electric current and a homogeneous magnetic field are applied to a particle-containing conductive fluid at crossed right angles to each other.^{12,13} The electromagnetophoretic migration velocimetry allows us to characterize the micro-particles in a liquid phase.^{13,14} Moreover, by using the high magnetic field generated by the superconducting magnet, electromagnetophoretic behavior allows for the chromatographic size separation method of particles,¹⁵ and the interaction force measurement of biological cells.^{16,17} However, in previous studies, this technique has been utilized only for solid particles. Moreover, the superconducting magnet is very effective, but its use for migration analysis was limited because the apparatus is large and expensive.

In the present study, we applied the electromagnetophoretic migration technique to a droplet-based system to develop a new analytical method for microdroplets. In addition, electromagnetophoretic migration velocimetry of organic droplets was

achieved with a simple and inexpensive setup by using permanent magnets to generate the magnetic field. The electromagnetophoretic migration velocity of 2-fluorotoluene microdroplets dispersed in 1.0 M KCl aqueous solution was measured to study the basic nature of electromagnetophoresis of organic droplets. Furthermore, to clarify the effect of surfactants on the electromagnetophoresis of microdroplets, 10^{-6} – 10^{-4} M of cetyltrimethylammonium bromide (CTAB) was added to the droplet-based system. The organic droplets were then characterized in terms of the amount of adsorbing surfactants on their surface by evaluating the surface conductivity of microdroplets calculated from electromagnetophoretic migration velocity.

Experimental

Chemicals

A supply of 2-fluorotoluene was purchased from Nacalai Tesque (Kyoto, Japan) and used as received. For the solution, 300 μl of 2-fluorotoluene was added to 5 ml of 1.0 M KCl aqueous solution, and then the mixture was sonicated for 2 min in a water bath in order to form micrometer-sized 2-fluorotoluene droplets in the aqueous solution. The dispersion of droplets could be maintained because the density of 2-fluorotoluene (1.004 g cm^{-3}) matches that of 1.0 M KCl. CTAB was purchased from Wako Chemicals (Japan) and dissolved in 1.0 M KCl aqueous solution to make a solution in the range from 10^{-6} to 10^{-4} M, in which 2-fluorotoluene was also dispersed. A suspension of polystyrene latex particles, with a diameter of 10 μm ($9.18 \pm 0.64 \mu\text{m}$), was purchased from Funakoshi (Tokyo, Japan). The polystyrene latex particles were dispersed in 1.0 M KCl solution ($2.7 \times 10^6 \text{ particles mL}^{-1}$). For the 1.0 M KCl solution used in our study as the medium, the values of electric conductivity and the fluid viscosity were 0.112 S cm^{-1}

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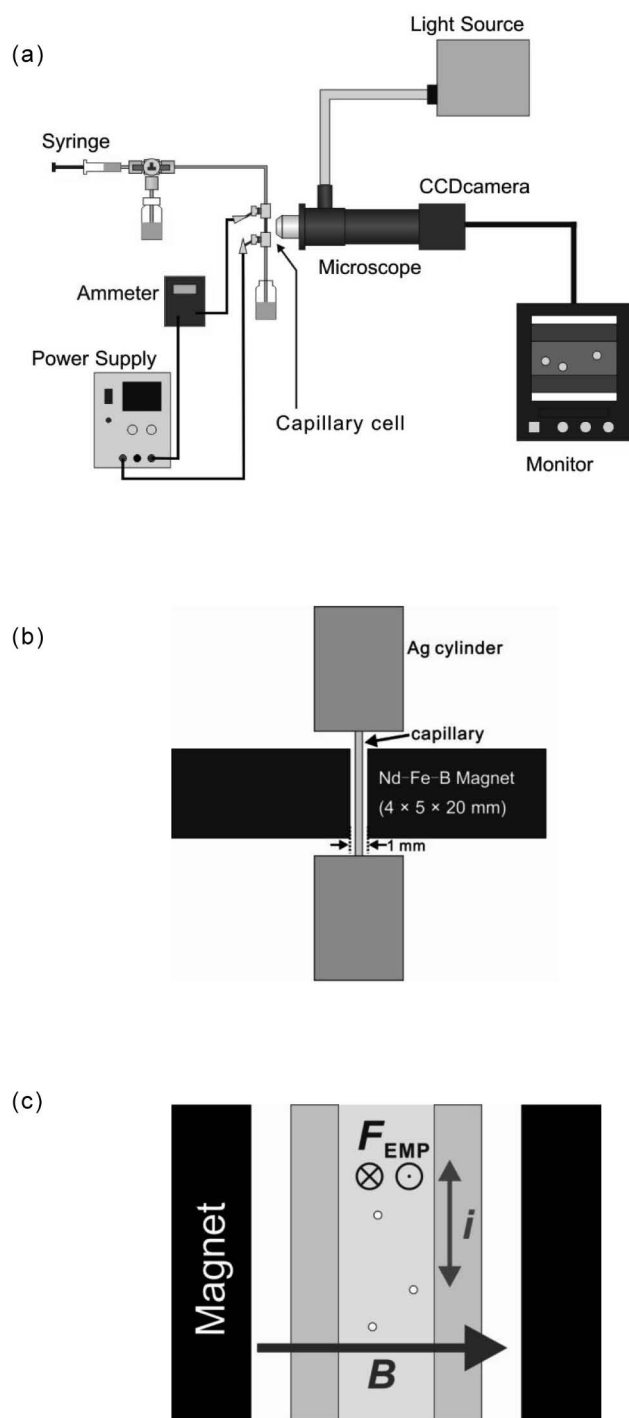


Fig. 1 Experimental setup for the measurement of electromagnetophoretic migration velocity of microdroplets. (a) Schematic drawing of the overall apparatus. (b) Configuration of capillary cell and two permanent magnets. Two Nd-Fe-B magnets were placed 1 mm apart from each other, and capillary cell was inserted between the permanent magnets. (c) Schematic drawing of the direction of applied fields and electromagnetophoretic force in the capillary cell.

and 0.88×10^{-3} Pa s, respectively.

Water purified by passing it through an EASYpure water purification system (Barnstead) had a resistivity of $18.1 \text{ M}\Omega \text{ cm}^{-1}$. The other reagents were used as received.

Apparatus and measurements

The electromagnetophoretic apparatus used in this study is shown in Fig. 1. The magnetic field was generated by square-shaped Nd-Fe-B permanent magnets (NeoMag, Japan) measuring $5 \times 4 \times 20 \text{ mm}$. Two permanent magnets were placed facing each other with a gap of 1 mm. The capillary cell was made from a square fused-silica capillary, with an inner section of $200 \times 200 \mu\text{m}$ and length of 10 mm. Both edges of the capillary were connected to PTFE tubes equipped with Ag cylinder electrodes whose inner surface was covered with AgCl generated by electrolysis in KCl solution. The capillary cell was placed between the two permanent magnets.

A potentiostat device (PL-250-0.3, MATSUSADA Precisions Inc., Japan) was used to provide the electric current, and the current was measured by an ammeter (Digital-multimeter VOAC7522, IWATSU, Japan). The migration behavior of the organic droplets was observed by optical microscope equipped with a CCD camera (WAT-231S, Watec, Japan). The CCD image was displayed on a monitor and also recorded on videotapes. The migration velocity and size of droplets were measured from image analysis.

The sample suspension was introduced into the capillary cell and then the electric current was applied for 3 s at 15 s intervals. The electromagnetophoretic velocity was calculated from the observed position of droplets in the cell upon every 3 s of current supply.

All measurements were carried out in an air-conditioned room at $25 \pm 1^\circ\text{C}$.

Results and Discussion

Theoretical discussion of electromagnetophoretic migration velocity

Under conditions of a homogeneous magnetic field and an electric current applied orthogonally to the solution, the net force of the electromagnetophoretic force, F_{EMP} , on a spherical particle can be written as:^{12,13}

$$F_{\text{EMP}} = 2 \left(\frac{\sigma_p - \sigma_f}{2\sigma_f + \sigma_p} \right) \frac{iBV}{S}, \quad (1)$$

where i is the electric current (A), B the magnetic flux density ($\text{N A}^{-1} \text{ m}^{-1}$), V the volume of the spherical particle (m^3), S the inner section of the cell (m^2), σ_f the electric conductivity (S m^{-1}) of the medium and σ_p the apparent electric conductivity (S m^{-1}) of the particle. The apparent conductivity of the particles can be determined from experimentally observed migration velocity using the theoretical equation:

$$v = \frac{4}{9} \left(\frac{\sigma_p - \sigma_f}{2\sigma_f + \sigma_p} \right) \frac{iBr^2}{S\eta} \quad (2)$$

where η is the fluid viscosity (Pa s), and r the radius of the spherical particle (m).

The apparent conductivity includes the surface conductivity of the particle. Any electric charge on the surface of the particle will produce an electric double layer. The ionic atmosphere around the particles yields the surface conductivity of the particles. Therefore, the apparent conductivity, σ_p , reflects the electrostatic surface property of the particle.¹³

Determination of the magnetic field

To determine the magnitude of the magnetic field produced by two permanent magnets in this system, we analyzed the

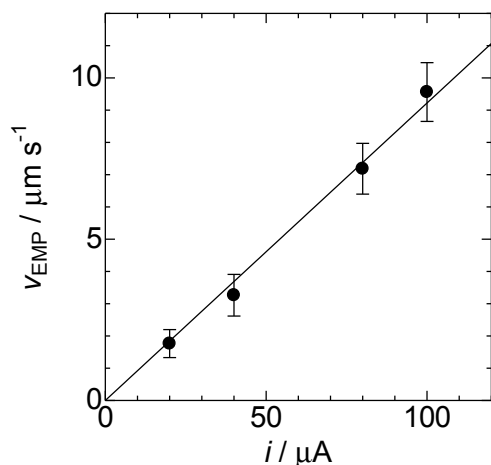


Fig. 2 Electromagnetophoretic velocity of polystyrene particles with a diameter of 10 μm , measured at various applied currents. A 1.0 M KCl solution was used as a conductive medium. The conductivity and the viscosity of the medium was 0.112 S cm^{-1} and 0.88×10^{-3} Pa s, respectively. The solid line shows the fitted lines derived from Eq. (2).

electromagnetophoretic migration velocity of the polystyrene particles whose electromagnetophoretic behavior was well documented. The current dependency of observed electromagnetophoretic migration velocity of polystyrene particles with a diameter of 10 μm is shown in Fig. 2. The magnitude of the magnetic field produce by two permanent magnets was calculated to be 1.0 T by applying Eq. (2) to the results shown in Fig. 2 using $\sigma_p = 0.019 \text{ S cm}^{-1}$. It was confirmed that a magnetic field of 1.0 T could be applied by our system using two permanent magnets, and the magnitude was enough to observe the electromagnetophoretic migration behavior of solid particles. We thus expect that our system can be applied to a droplet-based system.

Measurement of electromagnetophoretic migration velocity of 2-fluorotoluene droplets

We tried to observe the electromagnetophoretic migration behavior of 2-fluorotoluene droplets with a diameter of 8–12 μm dispersed in a 1.0 M KCl solution under the magnetic field of 1 T generated by two of permanent magnets. The organic droplets could be migrated by electromagnetophoretic force in a magnetic field of 1 T. The measured electromagnetophoretic migration velocity normalized to the unit radius was plotted against the applied current in Fig. 3. When the applied current was increased from 10 to 100 μA , the normalized migration velocity of 2-fluorotoluene microdroplets increased proportionally to the applied current, as expected in Eq. (2). The electromagnetophoretic technique was also applied to the microdroplets system in a similar manner as the solid particles system.

The solid line shown in Fig. 3 is the fitted curve derived from Eq. (1). The apparent conductivity of 2-fluorotoluene could be calculated to 0.029 S cm^{-1} with this fitted curve. The apparent conductivity of solid particles calculated by electromagnetophoretic migration velocity included surface conductivity caused by an electric double layer. In the case of organic droplets, an electric double layer also formed in an aqueous solution because the zeta potential of various organic emulsions in aqueous solutions was reported to be in the range from –10 to –80 mV.¹⁸ In addition, surface conductivity increased as the absolute value

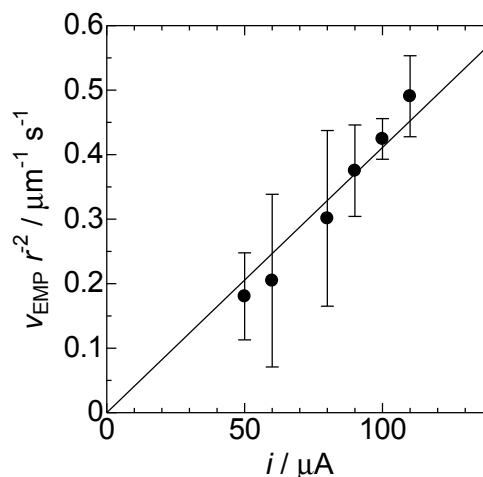


Fig. 3 The normalized electromagnetophoretic velocity of 2-fluorotoluene droplets with a diameter of 8–12 μm , measured at various applied currents. The magnitude of the magnetic field was 1 T. A 1.0 M KCl solution was used as a conductive medium. The solid line shows the fitted derived from Eq. (2).

of the zeta potential increased.¹⁹ Therefore, the apparent conductivity of organic droplets included surface conductivity levels similar to that of solid particles. Moreover, the apparent conductivity of 2-fluorotoluene droplets was of the same order of magnitude as that of polystyrene particles, and comparable with 0.025–0.050 S cm^{-1} reported for vesicles previously.²⁰ The apparent conductivity of organic droplets was governed by their surface conductivity and the obtained value was reasonable as the surface conductivity of organic droplets, because the zeta potential of polystyrene latex in 0.1 M KCl aqueous solution, which was reported to be about –25 mV, was comparable with those of organic emulsions.²¹ Our study thus suggests that organic droplets in the aqueous solution could be characterized by electromagnetophoretic migration velocimetry.

Electromagnetophoretic migration velocities of 2-fluorotoluene droplets with CTAB

Addition of surfactants to a droplet-based system may affect the stability and dispersibility of droplets because the surface properties of droplets are changed by the adsorption of surfactants to the surface of droplets.²¹ Therefore, we tried to evaluate the surface property of the droplets from their electromagnetophoretic migrations.

Figure 4 shows the current dependency of the measured electromagnetophoretic velocity normalized to the unit radius of 2-fluorotoluene droplets with a diameter of 10–16 μm dispersed in a 1.0 M KCl solution in the presence of CTAB with concentration range of 10^{-6} – 10^{-4} M. Generally, the migration velocity of organic droplets decreased as the concentration of CTAB increased in these measurements. The results suggested that the electromagnetophoretic migration velocity of organic droplets was influenced by the CTAB concentration in the medium.

The values of the critical micelle concentration and molecular surface area of surfactants at an interface were influenced by salt concentration in the bulk solution.²² It was reported that the molecular surface area of CTAB at the xylene/1.0 M NaCl solution interface was 0.48 nm^2 .²³ Taking account of this value and assuming that all 300 μl of 2-fluorotoluene was dispersed as droplets with the diameter of 12 μm , which was the average size

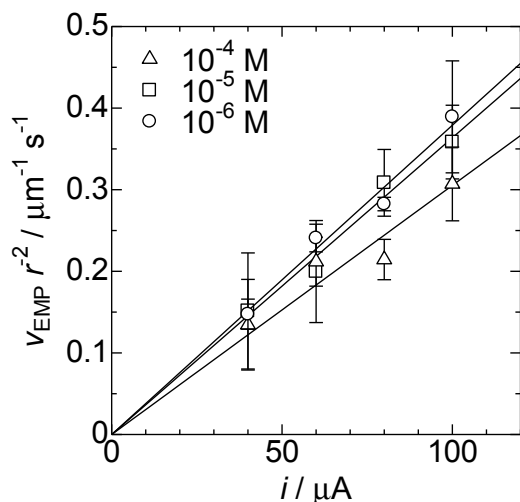


Fig. 4 The normalized electromagnetophoretic velocity of 2-fluorotoluene microdroplets with various CTAB concentrations in the range from 10^{-6} to 10^{-4} M at various applied currents. The magnitude of the magnetic field was 1 T. the conductive media used was 1.0 M KCl solutions containing CTAB. The solid line shows the fitted lines derived from Eq. (2).

of droplets measured in our experiments, in 5 mL of 1.0 M KCl solution, the molecular surface area of CTAB was calculated to be 0.50 nm^2 when all CTAB molecules included in 10^{-4} M solution adsorbed at the surface of droplets. This suggested that the amount of CTAB adsorbed at the surface of organic droplets had increased according to an increase in the CTAB concentration. Thus, it was considered that the electromagnetophoretic migration velocity of organic droplets was influenced by the CTAB concentration in sample solutions.

Figure 5 shows the apparent conductivities of 2-fluorotoluene droplets calculated from applying Eq. (2) to the results shown in Fig. 4 plotted against the negative logarithm of the CTAB concentration. The solid line indicates the value of 0.027 S cm^{-1} , which was the apparent conductivity of 2-fluorotoluene without CTAB. The apparent conductivities of 2-fluorotoluene droplets with 10^{-6} , 10^{-5} and 10^{-4} M CTAB could be obtained to 0.034, 0.037 and 0.046 S cm^{-1} , respectively. It was found that the apparent conductivity of 2-fluorotoluene droplets decreased and approached levels close to that in the absence of CTAB as the concentration of CTAB was reduced. Surface conductivity should increase as the concentration of CTAB rises because the zeta potential increases due to the adsorption of CTAB on the surface of emulsions.^{19,24} Thus, the tendency of the apparent change in the conductivity of 2-fluorotoluene droplets to the CTAB concentration was in good agreement with this estimate of surface conductivity. At the same time, it was considered that the surface conductivity of microdroplets was influenced not only by the CTAB concentration, but also by the size of microdroplets. Therefore, in our experiment, each plot of observed migration velocities of droplets shown in Figs. 3 and 4 had large standard deviations. Hence, by limiting the size of the droplets to be observed, it would be possible to obtain more precise quantitative values of the surface conductivity of droplets, and to estimate the concentration of CTAB from the electromagnetophoretic migration velocity of droplets.

Consequently, it was demonstrated that the organic microdroplets could be characterized in terms of the amount of adsorbing surfactant on the surface of the droplets calculated

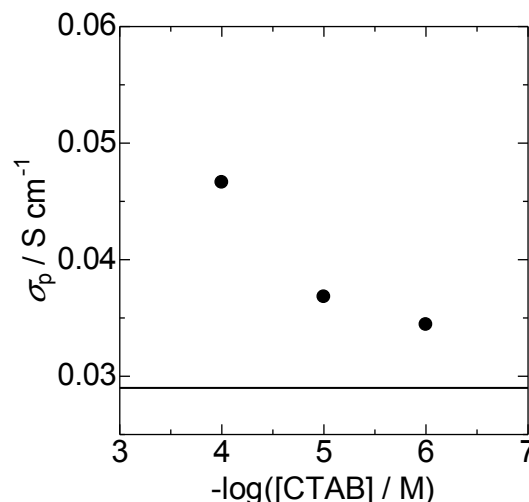


Fig. 5 The apparent conductivity of 2-fluorotoluene droplets with CTAB calculated from electromagnetophoretic migration velocimetry of microdroplets as a function of the negative logarithm of CTAB concentration. The solid line shows the value of the apparent conductivity of 2-fluorotoluene droplets in the absence of CTAB.

from the electromagnetophoretic migration velocimetry.

Conclusions

In the present study, we demonstrated that the electromagnetophoretic migration velocimetry of organic microdroplets was achieved in the magnetic field of 1 T generated by a pair of permanent magnets. In the magnetic field generated, the electromagnetophoretic migration velocity of organic droplets with a diameter of 8 – 16 μm could be measured. From the electromagnetophoretic migration velocimetry of 2-fluorotoluene droplets, the surface conductivity of 2-fluorotoluene could be estimated. Moreover, it was found that the electromagnetophoretic migration velocity of organic droplets was changed by adsorbing CTAB. Therefore, it was possible to characterize the organic microdroplets and to evaluate the amount of adsorbing surfactant on the surface of droplets based on electromagnetophoretic migration velocimetry. Thus, this technique is highly promising as a new method for analyzing microdroplets in droplet-based microfluidics system.

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