Zeta Potential Analysis of Submicron-sized Particles in Concentrated Suspension Using High-Intensity and High-Pulse-Rate Ultrasound

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1. Introduction

Zeta potential, which is a measure of stability of particle dispersion can be evaluated from electrophoretic velocity[1)]. The velocity has been measured using an optical microscope[2)] and the electrophoretic light scattering method[3)]. In our laboratory, we have developed the electrophoretic ultrasound scattering (ESS) method which allows us to measure structures in concentrated suspensions beyond the wavelength of visible light.

So far, the electrophoretic mobility of micron-sized particle in concentrated suspensions have investigated by the ESS method. Besides MHz-ultrasound being suitable to detect micron-sized particles, ultrasound does not have good sensitivity to nano- and submicron-sized particles because the wavelength of ultrasound is 100 times longer than that of visible light. Furthermore, there was a problem that particle mobility was overestimated due to high-energy ultrasound exerted on nanoparticles, so that we use low-intensity ultrasound to analyze nanoparticles. In this study, we propose a new analysis method which enables us to analyze quantitatively the electrophoretic velocity under influence of acoustic radiation pressure. Particularly, the electrophoretic mobility of 300 nm silica particles in concentrated suspensions was examined using high-intensity and high-pulse-rate ultrasound.

2. Experimental Section

2.1. Sample

Silica particles were purchased from Nippon Shokubai Co., Ltd., Japan. The nominal particle diameter was 300 nm. The silica particles were heated at 800°C for 8-24 hours in table-top muffle furnace (KDF-S70, Denken-HighDental Co., Ltd., Japan). After heat treatment, silica particles were dispersed in distilled water and the suspensions were sonicated for 5 minutes to disperse the particles uniformly.

2.2. Electrophoretic ultrasound scattering (ESS) method

A spike pulse at –275 V emitted from a BLP12R remote pulser (iSL, Japan) was transferred to a 40 MHz longitudinal focused transducer (Toray, Japan) immersed in a water bath to generate ultrasound pulses. The back scattered signals were received by the same transducer, followed by successive recording with a CSE1622 high-speed digitizer (Gage, DynamicSignals LLC, Canada). Such scattering signals were repetitively recorded 2,000 ~ 100,000 times at a constant time interval of 1 ~ 50 ms.

The sample cell of ESS measurement has the dimension 15×10×10 mm^3. Two platinum electrodes were fixed parallel to the cell wall. An arbitrary wave generator (Keysight Technologies, 33500B) produced a squared waveform with an amplitude of 0.2 ~ 2 Vp.p.. The period of squared wave was 20 seconds. The waveform was amplified 50 times by a high-speed high-voltage amplifier (9100A, Tabor, Israel) to produce 10 ~ 100 Vp.p. of the applied voltage.

2.3. Ultrasound scattering analysis

When the ultrasound pulse wave is irradiated onto the sample cell, the scattered wave containing the information of particle location was obtained. When the microparticles exhibit electrophoresis, the scattered amplitude, ψ varies with respect to the observation time, T. Therefore, the autocorrelation function of the amplitude variation was used to analyze the characteristic time. The normalized auto correlation function is calculated as follows:

$$g^{(1)}(\tau) = \frac{\langle \psi(t,T)\psi^*(t,T+\tau)\rangle}{\langle \psi(t,T)\psi^*(t,T)\rangle} \quad (1)$$

Particularly, when the particle displacement includes a mean component such as electrophoresis, the correlation function is given by,

$$g^{(1)}(\tau) = \cos(q\langle V\rangle\tau)\exp\left(-\frac{1}{2}q^2\langle \delta V^2\rangle\tau^2\right) \quad (2)$$

where $\langle V\rangle$ is the mean electrophoretic velocity, and

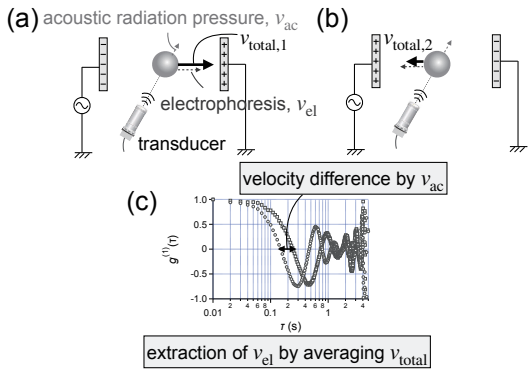

Fig. 1 Schematics of electrophoretic velocity accompanying acoustic radiation pressure with (a) the moving direction (a) approaching and (b) leaving from transducer. (c) is the correlation function obtained by the ESS method.

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$<\delta V^2>$ is the statistical dispersion of the velocity.

To analyze the dynamics of nano- and submicron-sized particles with high accuracy, it is necessary to use high-intensity and high-pulse-rate ultrasound. On the other hand, the acoustic radiation pressure, which is originated from high-energy ultrasound, may perturb the motion of particles[4]. In this study, an alternating voltage of low frequency wave was applied to suspension in order to independently evaluate the velocity of particle approaching and leaving from the transducer. **Fig. 1(a)** and **(b)** respectively show the particle motion involving effects of acoustic radiation pressure at the positive and negative voltage. The corresponding time correlation functions were shown in **Fig. 1(c)**. By averaging the magnitude of velocity obtained by the correlation functions, electrophoretic velocity can be evaluated because the effects of acoustic radiation pressure are cancelled out.

3. Results

Fig. 2 shows the pulse repetition time, PRT dependence of the electrophoretic velocity, $<V>$ normalized by the applied electric field, E of 300 nm silica particle. The $<V>/E$s at the negative and positive voltage exhibited the same value at the high PRT, but they deviated from the average value at the low PRT. These results suggested that the effect of the acoustic radiation pressure increased by effective ultrasound energy. The average velocity is shown in the solid markers in Fig. 2. Interestingly, it was confirmed that the average velocity was constant irrespective of PRT. Therefore, while the acoustic radiation pressure increased with intensity and pulse rate, it is suggested that acoustic radiation pressure could be cancelled out by averaging the velocity.

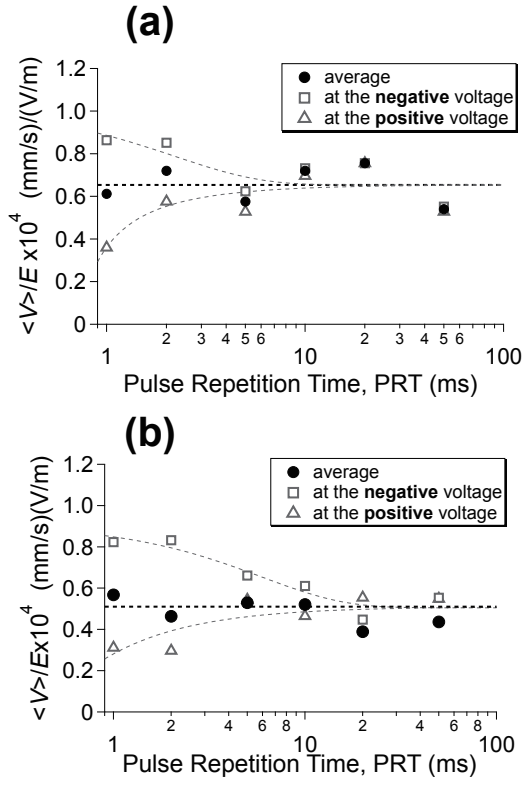

Fig. 2 The PRT dependence of the normalized electrophoretic velocity of 300 nm silica particle at (a)0.5wt%, (b)20wt%.

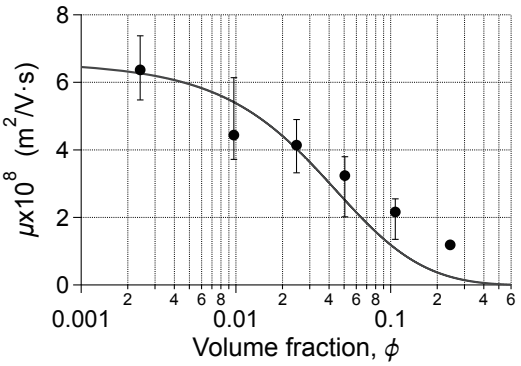

Fig. 3 The ϕ dependence of the μ of 300 nm silica particle. The solid line is the theoretical prediction of the μ in concentrated suspension[5~7].

Fig. 3 shows the volume fraction, ϕ dependence of the electrophoretic mobility, μ obtained for the 300 nm silica particle. The μ decreased with increasing the particle concentration. At the high concentration, the electric field surrounding a particle must be considered to evaluate the effective mobility. Such a consideration was made by effective medium models[5~7]. As shown in the solid line, the experimental data was well reproduced by the models.

4. Conclusion

The electrophoretic velocity of 300 nm silica particle was investigated by using focused beam transducer with high-pulse-rate ultrasound. Though the difference of the velocities at the negative and positive voltage increased with decreasing PRT due to acoustic radiation pressure, the electrophoretic mobility was obtained by averaging the velocities by cancelling out acoustic radiation pressure.

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