Electrophoretic Mobility Analysis of Submicron-sized Microparticles in Concentrated Suspension Examined by Electrophoretic Ultrasound Scattering Technique

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1. Introduction

The surface charge properties of microparticle are often considered as a measure of homogeneity and stability of particle dispersion in suspension because the effective surface charges promote a strong repulsion between microparticles in aqueous suspension[1]. Electrophoretic mobility and zeta potential have been evaluated by the microscopic electrophoresis under microscope observation or the electrophoretic light scattering (ELS) method. On the other hand, measurement of concentrated samples and/or structures beyond the wavelength of visible light requires considerable dilution. Also, since the wavelength of megahertz ultrasound is about 100 times longer than that of light, ultrasound is suitable for submicron and micron size particle measurements, and it can be applied to measurements of concentrated systems. In this study, we investigated the electrophoretic mobility of concentrated suspensions and submicron particles by electrophoretic ultrasonic scattering methods to establish a measurement technique for concentrated systems of particle suspension.

2. Experimental section

2.1. Sample

Silica particle was purchased from Nippon Shokubai Co., Ltd., Japan. The nominal particle diameter was 500 nm. Silica particles were heated at 800°C for 8 hours in a 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) Technique

A spike pulse emitted from BLP12R remote pulser (iSL, Japan) was transferred to a 20 MHz longitudinal plane wave transducer (KGK, 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 10,000 times at a constant time interval of 5, 10 or 15 ms the particle motion. The sample cell of the ESS measurement has the dimension 15 × 10 × 10 mm^3. Two platinum electrodes were fixed parallel to the cell wall. Arbitrary wave generator (Keysight Technologies, 33500B) produced a sinusoidal waveform or squared pulse waveform with an amplitude of 1 or 2 V. The period of sinusoidal wave was 3 or 10 seconds. These waveforms were amplified 50 times by a high-speed high-voltage amplifier (9100A, Tabor, Israel) to produce 50 or 100 V of the applied voltage.

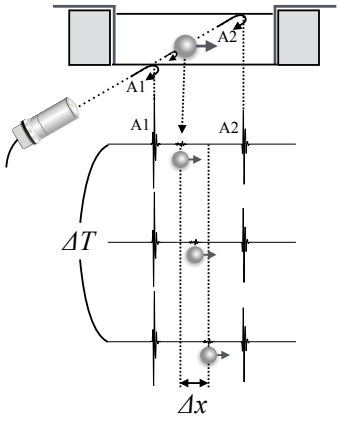

Fig. 1 Schematic illustration of the two reflected echoes observed by ultrasound measurement.

When the ultrasound pulse wave is irradiated onto the sample cell, two reflected echoes from the cell wall were observed (**Fig. 1**). For particle suspensions, scattering signals are observed between A1 and A2. The particle displacement, $\Delta x = \Delta\theta / q$ in suspension is obtained by the ultrasound scattering analysis of the scatted wave phase θ at a fixed scattering vector q during the observation time, T. Then, the electrophoretic velocity of particles, V can be calculated from Δx and ΔT by repetitively emitting ultrasound pulse as a function of the sample depth[2]. The electrophoretic mobility μ, i.e., V divided by the electric field, was employed in the analysis.

3. Results

The volume fraction dependence of the electrophoretic mobility, μ of the silica particles of 500 nm diameter is shown in **Fig. 2**. Since the ELS method is suitable for measuring relatively dilute systems, measurements were started at 0.001vol% and extended to about 1vol%. At the higher concentrations, visible light could not transmit

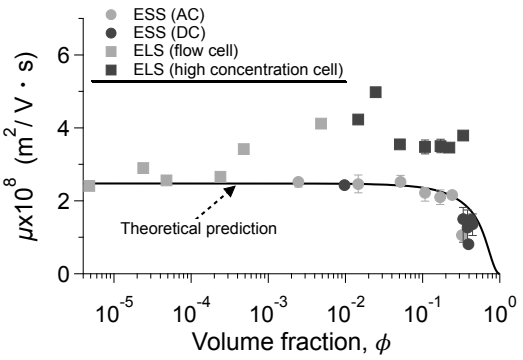

Fig. 2 ϕ dependence of μ obtained by the AC-ESS method (gray circle), the DC-ESS method (black circle), and the ELS method equipped with a flow cell (gray square) and a high concentration cell (black square). The solid line is the theoretical prediction[3].

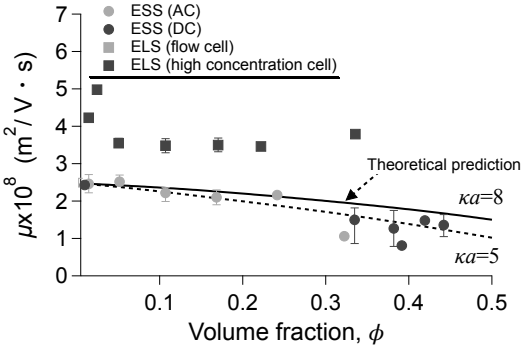

Fig. 3 Detail view of Fig. 2. Solid line is the theoretical prediction using κa=8 (calculated) and dashed line is theoretical prediction using κa=5.

through the suspension, so a high concentration cell was used. In this cell, the optical path length was shortened to allow measurement of concentrated suspensions using light which slightly penetrated into the sample cell. The ELS measurements were carried out up to 30vol% by the sample cell. In the ESS method, measurements were carried out using alternate current (AC) and direct current (DC) voltages. The concentrated suspensions require significantly longer time than the dilute suspensions to observe a stable electrophoretic velocity data because of the viscosity or reduction of the effective electric field. Thus, in concentrated suspensions, the measurements were conducted with the DC method rather than with the AC method with a reduced frequency to shorten the measurement time.

Compared to the ELS method, the ESS method was suitable for the concentrated suspensions. Particularly, the novel ESS method allowed us to measure the concentrated submicron particle suspensions up to 45vol% for the first time. The μ of the dilute system of the ELS method and the dilute system of the ESS method were the almost equivalent, although each technique probes the different concentrations. In addition, the theory[3] predicts that the μ below 10vol% is independent of the particle volume fraction. However, there was a systematic difference between the ELS data and the theoretical prediction above 0.1vol%. The ELS method became difficult to evaluate the correct μ as particle concentration increased. In addition to the multiple scattering effects, since the particle diameter, 500 nm is equivalent to the wavelength of light, the analysis becomes difficult without considering the structure factor associated with the intraparticle interference. However, for the ELS method, it was not allowed because of the fixed wavelength and fixed angle measurements. On the other hand, the μ obtained by the ESS method decreased gradually as the particle concentration increased, and the μ was close to the theoretical prediction. Thus, it was suggested that ultrasound can be used to measure electrophoretic mobility of submicron particles over a wide range of concentrations. However, as shown in **Fig. 3**, the μ obtained by the ESS method was slightly lower than theoretical prediction at concentrations above 32vol%. Interestingly, according to a literature, ELS measurements of 50 nm polyurethane particles exhibited a similar disagreement between the experiments and the theory[4]. While a disagreement was found at the realistic value of κa=5, where a is the particle radius and κ^{-1} is the Debye screening length, the theoretical curve seemed to fit the experimental data well when κa=2.5 was used although it was smaller than the expected property. For our 500 nm silica particles, by decreasing κa from κa=8 to κa=5, the theoretical curve matched the experimental results. Such a contradiction of the κa parameters suggested that the further consideration of overlapping electrical double layer thicknesses or hydrodynamic interactions is required in the theory at the concentrated regime.

4. Conclusion

The electrophoretic mobilities, μ of silica particles of 500 nm diameter from dilute to concentrated suspension were investigated by the electrophoretic ultrasound scattering (ESS) and electrophoretic light scattering (ELS) method. μ evaluated by the ELS method deviated from the theoretical prediction above 0.1vol%, while the agreement between the ESS data and the theoretical prediction was confirmed up to 32vol%.

References

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