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Size-selective separation of submicron particles in suspensions with ultrasonic atomization

Susumu Nii *, Naoyoshi Oka

Department of Chemical Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

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ABSTRACT

Aqueous suspensions containing silica or polystyrene latex were ultrasonically atomized for separating particles of a specific size. With the help of a fog involving fine liquid droplets with a narrow size distribution, submicron particles in a limited size-range were successfully separated from suspensions. Performance of the separation was characterized by analyzing the size and the concentration of collected particles with a high resolution method. Irradiation of 2.4 MHz ultrasound to sample suspensions allowed the separation of particles of specific size from 90 to 320 nm without regarding the type of material. Addition of a small amount of nonionic surfactant, PONPE20 to SiO_2 suspensions enhanced the collection of finer particles, and achieved a remarkable increase in the number of collected particles. Degassing of the sample suspension resulted in eliminating the separation performance. Dissolved air in suspensions plays an important role in this separation.

1. Introduction

Irradiation of a high frequency ultrasound in megahertz-range to a liquid brings about atomization into very fine droplets whose sizes are micrometer or below with a narrow size distribution. Unlike conventional pneumatic atomizers, no high pressure and orifice is required in this simple method, and formation of coarse droplet is successfully suppressed. Size of liquid droplets is tunable by varying the ultrasonic frequency and physical properties of liquids [1]. Because of the advantage of producing size-controlled droplets, the method has been applied to inhalation drug delivery [2,3], fuel combustion [4] and analytical nebulizers [5]. The method was even useful for fabricating nanostructured materials [6,7] or nanocomposits, where the liquid droplets are 'mother' of the products.

We had an idea of using the droplets as containers for solid particles of a specific size to be separated from its suspension. Possibility of the idea was proven by the authors with aqueous suspensions of silica and bentonite [8]. Sato's report [9] of ethanol separation from its aqueous solution triggered our interest in applying ultrasonic atomization to separation. They have shown a preferential distribution of ethanol between bulk liquid and fog. Prior to their report, Rasshokin [10] had published the enrichment of a surfactant into the droplets ultrasonically atomized. No such distribution occurs in conventional atomizers, where the whole liquid is atomized. Since after the recognition as a separation technique, ultrasonic atomization has been studied extensively on separating other materials such as alcohols [11], surfactants [12], amino acids [13], and carbon nanotubes [14].

The present study focuses on deeper understanding of the separation of submicron particles of silica or polystyrene latex from suspensions. Our motivation is to develop an easier and simpler method than conventional ones. Summarized in a review article by Fedotov et al. [15] were common methods for separating micrometer- to nanometer-sized particles in analytical chemistry. Generally, ultrafiltration and microfiltration were performed in which membranes were used as a barrier for particles. In field-flow fractionation, a thin channel for liquids is provided and fluid flow is finely designed [16]. A physical force field such as gravitational, centrifugal or electric is applied to enhance separation. Microfluidic systems use confined space for sieving or controlling particle movement in fluids [17–19]. Methods depending on narrow paths for fluids suffer from a serious problem of clogging and pretreatment of crude samples is required for a stable operation. Furthermore, the particle concentration of the sample is limited to low. Even in centrifugal sedimentation [20], which has been applied to larger scale processes, finding a suitable density gradient is difficult. In contrast, ultrasonic atomization is free from difficulties in narrow paths or finding additives for making density gradient, and it could be robust for crude samples. The method is potentially useful for practical particle separation.

* Corresponding author. Tel.: +81 527893390; fax: +81 527893269.
E-mail address: nii@nuce.nagoya-u.ac.jp (S. Nii).

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To enhance characterization of this separation method, solid particle size and its concentration were finely evaluated with equipment enables a high resolution analysis. Also, an approach, degassing of the sample suspension was adopted to shed a light on the mechanism.

2. Experimental

Solid samples employed in this study are size- and shape-controlled SiO_2 (Sicastar, micromod Partikeltechnologie GmbH) and polystyrene, PS, latex particles (Micromer, micromod Partikeltechnologie GmbH). The shape was spherical, and the sizes for SiO_2 particle are four different nominal diameters of 50, 70, 100, and 300 nm. The diameters for PS latex particles are 50 and 100 nm. Sample suspensions were prepared by mixing two types of particles of the same material with different sizes in a predetermined volume of deionized water. In the preparation, the number of particle for each diameter was set to be close, and total particle concentration was set constant at 1000 ppm. This particle concentration is much higher than the conditions taken in reported studies on separation of nanometer-sized particles [21–23].

A surfactant, polyoxyethylene(20) nonylphenylether, PONPE20 was used as an additive to modify the separation performance.

Particle-size distribution of the solid sample was measured with a method of tracking analysis of particles illuminated by a laser light. The apparatus used was Nanosight LM-10R (Quantum Design Japan Co. Ltd.). The method enabled us an observation of individual particles as point-scatterers moving under Brownian motion. Basic principle of size determination is based on Stokes–Einstein's equation. Such a direct observation of particle suppresses background effect, thus attained were both a high resolution and a measurement of concentration of solid particles. Lower detection limit of particle diameter is 30 nm (depending on the sample property) [24].

A schematic diagram of the experimental apparatus is shown in Fig. 1. It consists of an atomization column and a particle collection unit. The column is 0.25 m in height and 0.054 m in diameter. To irradiate an ultrasound with a frequency of 2.4 MHz to sample suspensions, a transducer whose diameter of 0.02 m was mounted at the bottom of the column. A suspension sample with a volume of 50 cm^3 was irradiated with the ultrasound at a constant electric power input of 10 W. Temperature of the suspension was kept constant at 303 K by cooling with a coolant flowing in the coiled tube. As was observed in most liquids, the ultrasonic irradiation to suspensions led to the formation of a fountain. A fog containing solid particles was formed at the surface of the fountain. The fog was taken out of the column by nitrogen flowing at a rate of 0.5 L/min, and was transferred to the particle collection unit for 1 h. In the unit, the fog and nitrogen were passed through an impinger loading with 30 cm^3 of water to capture solid particles. Another type of equipment, a cold trap using liquid nitrogen was also applied for collecting particles.

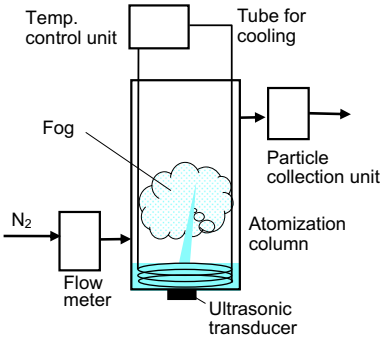

Fig. 1. Schematic diagram of experimental apparatus.

3. Results and discussion

3.1. Separation of mixtures containing SiO_2 particles

A typical experimental result was presented in Fig. 2, where the particle concentration is plotted against the diameter. The sample suspension consists of 100 and 300 nm SiO_2 particles. Two main peaks for 100 and 300 nm particles were detected, which means a high resolution of the present analysis. Concentrations of collected particles were much lower than the sample suspension due to dilution which is inevitable in the collection method. The impinger method is simple but uses water as a medium for particle collection, and fog is brought into contact with water. In spite of a high stability of observed values, concentration of collected particle depends largely on conditions such as water volume, shape of the reservoir and method of dispersing gas. Therefore, another method, a cold trap with liquid nitrogen was applied to confirm the evaluation with impinger method and also to find actual solid particle concentration in fog. The cold-trap method attained a fog collection rate of 80 wt%, and particle concentration was found to about 40% of the original sample, which is much higher than approximately 0.1% from impinger method. Particle size distributions for both collection methods were compared in Fig. 3. Two curves accorded well with a small difference in diameter, thus the result assured validity of the impinger method. Due to the simplicity in operation, impinger method was applied for size determination of particles and relative evaluation of particle concentration.

Collected particles mainly consisted of 100 nm particles. The size distribution was shown in Fig. 4. The median diameter of the collected particles was 140 nm. The result clearly demonstrates that the smaller particles were selectively transferred into fog.

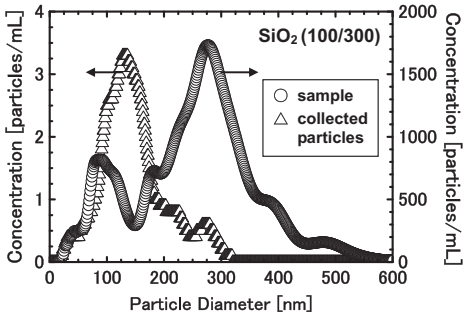

Fig. 2. Concentration of particles contained in original sample mixture of SiO_2 (100 and 300 nm) and of collected particles.

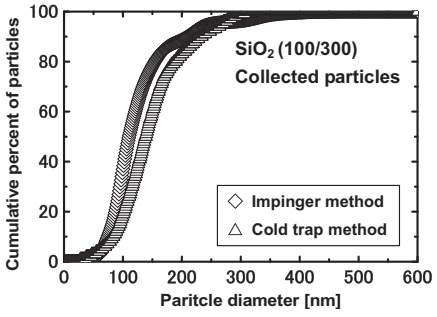

Fig. 3. Comparison between particle size distribution of collected particles with impinger and cold trap.

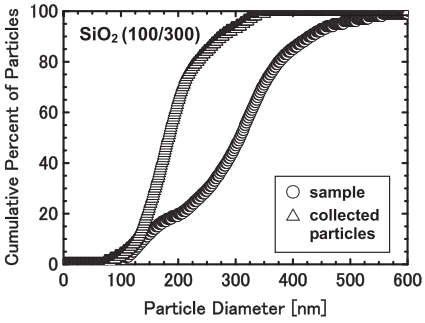

Fig. 4. Particle size distribution of sample suspension of SiO_2 (100 and 300 nm) and collected particles.

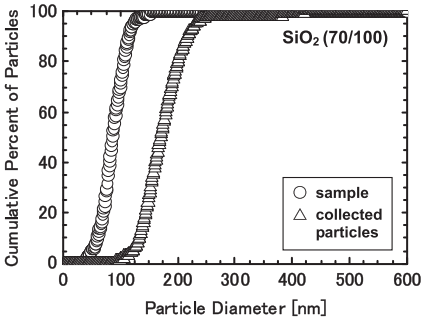

Fig. 6. Particle size distribution of sample suspension of SiO_2 (70 and 100 nm) and collected particles.

Those solid particles can be included in mist; however, it is still uncertain whether such an inclusion is a dominating mechanism as will be discussed later.

Fig. 5 demonstrates concentration of collected particles and that of sample suspension containing 70 and 100 nm particles. Smaller particles whose size is mainly 70 nm were rejected and the larger particles, mainly 100 nm in diameter were collected. There should be no effect of agglomeration or fragmentation of SiO_2 particles on this result. As discussed in our previous study using the same SiO_2 material [8], SiO_2 has a high negative charge in the present pH range of 5–6. Also, in our preliminary experiment using a sample containing single-sized particle, no change was observed in size distribution of sample and collected particles. The cumulative percent of the particles were plotted in Fig. 6. The result indicates that very sharp separation was attained, and particles larger than 90 nm were collected. When both results of Figs. 4 and 6 were taken into account, SiO_2 particles whose sizes in the range of 90–320 nm are brought into fog by the atomization. Ultrasonically prepared fog 'recognizes' the size of solid particles to be transferred into gas phase. The particle size does not correspond to the reported result of the peak diameter of water droplet produced by ultrasonic irradiation at 2.4 MHz. The authors [23] have applied a laser diffraction method and reported that a number-averaged diameter of water droplets was around 5 μm, which was comparable to the predicted diameter with Lang's equation [25], 2.3 μm. It should be noted that the detection limit of the analytical instrument was 500 nm. When it was assumed that solid particles were included into water droplets having a closer size of the solid particle, there should be a large amount of water droplets smaller than the detection limit of 500 nm with a narrow size distribution. Due to the lack of the evidence, the separation mechanism remains unclear. A method which enables us to recognize solid and liquid particles separately and to detect particles less than 500 nm will be a strong tool for further understanding of the separation mechanism.

3.2. Separation of mixtures containing PS latex

To examine the applicability of this separation method to other materials, aqueous suspension of PS latex containing 50 and 100 nm particles was ultrasonically atomized. The result was shown in Fig. 7 as a cumulative particle size distribution. The median diameter of the collected particles was 150 nm. The same trend as for SiO_2 suspension containing 70 and 100 nm particles was observed for PS latex. It should be noted that no particle agglomeration occurred for this sample. In the preliminary experiment using single-sized particles, no change was found in size distribution between sample and collected particles. The size distribution curve for collected PS particles was closely accorded with that for SiO_2 particles shown in Fig. 6. Such a good agreement in the trend of separation might suggest that the role of chemistry is less significant in this separation, but the size has a stronger effect. A certain physical process is probably relating with the separation.

3.3. Controlling the separation performance

Our previous study [8] showed that the addition of a surfactant, SDS lowered the size of collected particles, and also narrowed the peak width of the distribution curve. In the present study, a non-ionic surfactant, PONPE20 was added to SiO_2 sample suspension containing 100 and 300 nm particles to examine the effects on separation characteristics. Cumulative size distribution of collected particles for different concentrations of PONPE20 was plotted in Fig. 8. Even though peak sharpening and shifting to lower size were observed in size distribution as same as the case for SDS addition, the concentration was less than four orders of magnitude. Addition of PONPE20 at very small concentration effectively lowers the size of collected particles and also narrows the size distribution.

Furthermore, the addition of PONPE20 significantly enhanced particle collection. Fig. 9 represents concentration of collected

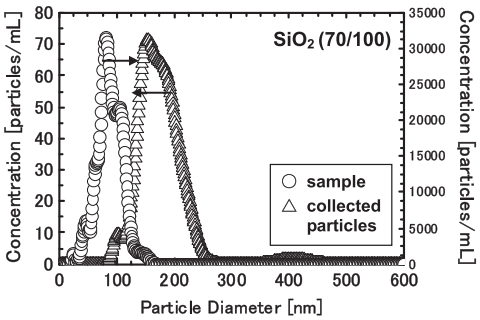

Fig. 5. Concentration of particles contained in original sample mixture of SiO_2 (70 and 100 nm) and of collected particles.

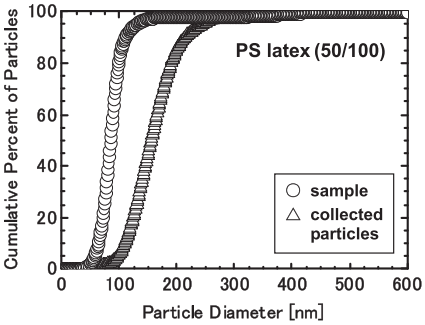

Fig. 7. Particle size distribution of sample suspension of PS latex (50 and 100 nm) and collected particles.

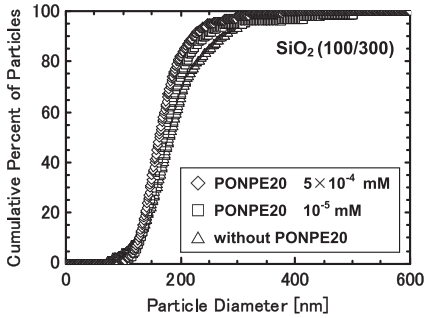

Fig. 8. Effect of PONPE20 concentration on particle-size distribution of collected particles from sample containing SiO_2 (100 and 300 nm).

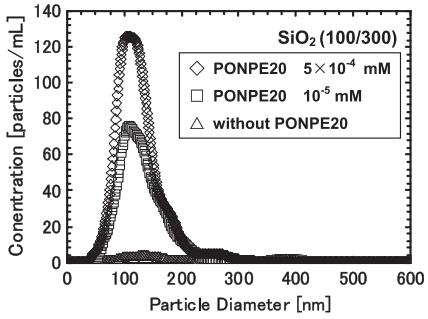

Fig. 9. Effect of PONPE20 concentration on number concentration of particles collected from sample mixture of SiO_2 (100 and 300 nm).

particles for different PONPE20 concentration. Due to dilution effect of impinger method as discussed in Section 1, values of concentration were much smaller than actual particle concentration in fog. Thus, relative evaluation of particle concentration is more meaningful than evaluation with absolute value of concentration. Even at a little addition of PONPE20 to 10^{-5} mM, the concentration reached the value of 26 times higher than that without surfactant. Further addition to 5×10^{-4} mM doubled the concentration attained at 10^{-5} mM. From a practical viewpoint, this finding intensifies the potential of this separation because the efficient collection of target particles is a key issue in the processing.

Reason for the enhancement of particle collection by the surfactant addition is yet unclear, further study is required for elucidation. It should be closely relating with the mechanism of selective transfer of particles from bulk liquid to gas phase through fog formation. The presence of cavitation bubbles in the fountain jet under ultrasonic atomization has been observed by several researchers [26,27]. Recently, a high speed image for ultrasonic atomization of water with the irradiation of 1 MHz was presented by Choi et al. [28] and they also pointed out the presence of cavitation bubbles in the fountain jet.

3.4. Relation between particle separation and dissolved gas

As was suggested by Boguslavskii and Eknadiosyants [26], cavitaion is possibly playing a role in ultrasonic atomization, and cavitation bubbles might be in sample suspension when the fog formation. Then cavitation may also relate with the particle separation with ultrasonic atomization. To examine the possibility, the air-saturated sample suspension was degassed by reducing pressure. Removal of 90% of dissolved oxygen, DO, was attained by the degassing. Oxygen concentration was analyzed with a DO meter and the amount of oxygen corresponded to air content in the medium. An experiment was conducted with the degassed

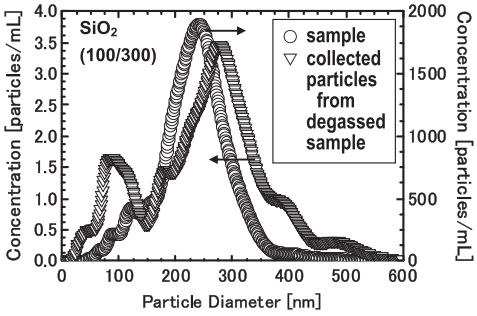

Fig. 10. Effect of degassing of sample suspension on number concentration of particles collected from sample mixture of SiO_2 (100 and 300 nm).

sample containing SiO_2 of 100 and 300 nm, and the result was presented in Fig. 10. Remarkably, no separation occurred from the degassed sample. Size distribution for the collected particle was very similar to that for the original sample. Although the elimination of cavitation bubbles was uncertain under the present condition, this finding clearly suggests that dissolved gas plays a major role in the particle separation. Further study is required to elucidate the gas's role in the separation mechanism.

4. Conclusion

Solid particles of SiO_2 or polystyrene whose size is in a limited range were successfully separated with ultrasonic atomization, and the size of collected particles was analyzed with a high resolution method. Irradiation of 2.4 MHz ultrasound to sample suspensions allowed to separate particles in the range of 90–320 nm without regarding the type of material. Addition of a nonionic surfactant, PONPE20 to sample SiO_2 suspensions resulted in collecting finer particles, and achieved a remarkable increase in the number of collected particles. Degassing of sample suspension eliminated the performance of particle separation.

Acknowledgement

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