Correlation between Acoustic Cavitation Noise and Yield Enhancement of Sonochemical Reaction by Particle Addition

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The mechanism of the effect of particle addition on sonochemical reaction is studied through the measurements of frequency spectrum of sound intensity for evaluating the cavitation noise and the absorbance for the liberation of iodine from an aqueous solution of KI as an index of oxidation reaction by ultrasonic irradiation in the presence or absence of alumina particles. As it is expected that both the acoustic noise and a rise in temperature in the liquid irradiated by intense ultrasound will increase with the number of collapsing bubbles, these are supposed to be the best tools for evaluating the relative number of bubbles. In the present investigation, it has been shown that the addition of particles with appropriate amount and size results in an increase in the absorbance when both the acoustic noise and the rise in the liquid temperature due to cavitation bubbles also increase. This suggests that the enhancement in the yield of sonochemical reaction by appropriate particle addition comes from an increase in the number of cavitation bubbles. The existence of particle in liquid provides a nucleation site for cavitation bubble due to its surface roughness, leading to the decrease in the cavitation threshold responsible for the increase in the number of bubbles when the liquid is irradiated by ultrasound. Thus, from the present investigation, it is clarified that the particle addition has a potential to enhance the yield in the sonochemical reaction.

1. Introduction

Chemical reaction with oxidants of hydroxyl radical, ozone, hydroxyl peroxide, etc. from hot spot at violent collapse of cavitation bubbles in liquid irradiated by intense ultrasound is referred to as a sonochemical reaction.[1] Sonochemical reactions are promising for novel material synthesis, environmental treatment, biological application, etc. Although the sonochemical reaction field has uniqueness of high temperature of several thousand Kelvin, high pressure of about 1000 atm, and rapid heating and cooling rates of 10^{10} K/s inside the bubbles at the violent collapse as compared to other processes, an optimization of sonochemical reaction field based on the increase in the number of cavitation bubbles to accomplish high efficiency in the reaction is required for actual use in industry.

Recently, it has been suggested that the broadband component in the frequency spectrum of the acoustic noise, which is called "white noise", has an intensity which corresponds to the number of cavitation bubbles active in chemical, physical, and biological processes.[2,3] The white noise is caused by the strong nonlinear pulsations of bubbles such as shock wave emission from bubbles and acoustic emission from chaotically oscillating bubbles.

Particle addition has a potential to enhance the yield in the sonochemical reaction.[4,5] The existence of particle in liquid provides nucleation site for cavitation bubble due to its surface roughness leading to the decrease in the cavitation threshold when the liquid is irradiated by ultrasound.[6−8] It is expected that such particle addition results in an increase in the number of bubbles; however, it has not been proved so far whether the increase in the number of bubbles due to particle addition is responsible for the enhancement in the yield of sonochemical reaction.

Particle addition has the probability to increase the temperature of the liquid irradiated by ultrasound, because the increase in the number of bubbles due to the effect as described above results in an increase in the heat conducted from hot spot inside collapsing bubbles to bulk liquid together with a friction between the liquid and the bubbles in oscillation. Pioneer scientists in the field of sonochemistry in Japan, Oyama et al.,[9] have detected a rapid increase in temperature in the liquid containing crystal particles ranging from 2 to 35 μm in size when they inserted a thermocouple into the liquid just after the sonication. However, the reason for such an increase in temperature was not identified. In addition, there has been no report so far for an influence of the amount of gas dissolved in a liquid on the increase in temperature.

In this report, a mechanism for the effect of particle addition on sonochemical reaction is studied through the measurements of frequency spectrum of sound intensity for evaluating the acoustic white noise and the absorbance for the liberation of iodine from an aqueous solution of KI[10,11] as an index of oxidation reaction by ultrasonic irradiation in the presence or absence of alumina particles. Also, the time history of temperature in degassed or air-saturated liquid irradiated by ultrasound is measured in the presence or absence of alumina particles.

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2. Experimental Section

For the measurements of I_3^- absorbance, acoustic cavitation noise, and liquid temperature as described below, the amount of liquid used in each case was 1 mL prepared in 13 × 100 mm disposable Pyrex tubes (IWAKI GLASS Ltd.) fixed at the center of a bath-type reactor (Branson, 1510J-MT, 42 kHz, nominal total electric power 70 W) filled with degassed water. All of the particles used for addition were alumina (Al_2O_3).

2.1. Measurement of Absorbance of I_3^-. Ultrasonic irradiation into an aqueous KI solution results in the oxidation of I^- ions to give I_2, which react with I^- to form I_3^- ions in the presence of excess I^- ions.[10,11] In the present experiments, absorbance measurements were carried out with a spectrophotometer (JASCO, V-530) within the range from 300 to 500 nm including the absorbance peak of I_3^- at 352 nm.[12]

The experimental procedure for KI oxidation by sonication under particles addition is as follows: 1 mL aqueous KI solution (0.1 mol dm^{-3}) kept at 20 °C was bubbled by air for 30 min before sonication. The dissolved oxygen content in the solution before sonication was made to 8.8 mg dm^{-3} (air-saturation). Alumina particles (Al_2O_3) of various sizes and amounts were used as the additive into the solution to investigate the particle-size dependence and the particle-amount dependence of sonochemical reaction. The solution was sonicated for 60 s. After sonication, the particles were removed by a centrifuge, and the absorbance of the clear layer at the top of the sample was then measured. The peak value of the absorbance was measured at various sizes and amounts of the added particles.

2.2. Measurement of Acoustic Noise. Frequency spectra of acoustic noise from air-saturated/degassed water with/without the alumina particles were measured. The acoustic noise was measured by a hydrophone (RESON, TC4038), which was immersed in a tube containing water. The noise was transformed to the frequency spectrum by the spectrum analyzer (SONY Tektronix, 3026) with the averaging operations of 100 times. Before sonication, the dissolved oxygen content in the solution was made to almost air-saturated (8.6 mg dm^{-3}), or degassed (1.5 mg dm^{-3}), which does not result in any cavitation. The particles used were the same particles as those in the absorbance measurements. The mean particle size was about 10 μm in diameter, and the amount was 20 mg, where the size and the amount were selected appropriately obtained from the results in the absorbance measurements for the enhancement of sonochemical reaction.

2.3. Measurement of Time Evolution of Liquid Temperature. Liquid temperature was measured for every 1 s during 30 s (rest time) before sonication followed by 60 s sonication with a thermocouple (Advantest S Theath thermocouple TR1101-1300, K-type, 1.6 mm) immersed at the center of the liquid. The conditions applied for the liquid of air-saturated/degassed water and the particles used (10 μm and 20 mg) were the same as in the measurements of acoustic noise.

3. Results and Discussion

Figure 1 shows the particle-amount dependence of the absorbance ratio of an aqueous KI solution with alumina particles (Al_2O_3) to that of a solution without alumina particles following sonolysis. For this case, the size of particles was fixed to 10 μm. The plotted data were averaged over three times. It can be observed that, when the amount of alumina particles increased up to 20 mg, the absorbance also became higher than for the control in absence of particles. This is because, with an increase in the added amount of particles, the sum of surface area also increases. Increase in the surface area could contribute to provide nucleation sites of bubbles active for sonochemistry. When the added amount of particles increased more than 20 mg, however, the absorbance became lower. This is caused by the substantial prevention of sound propagation due to the increase in the number of particles.

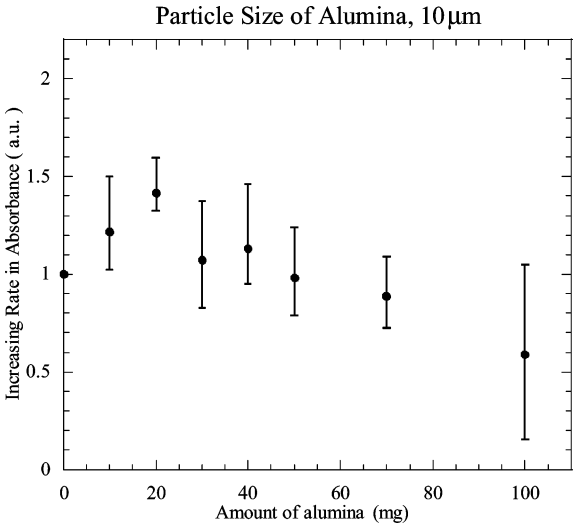

Figure 1. Particle-amount dependence of the absorbance ratio of an aqueous KI solution with alumina particles (Al_2O_3) to that of a solution without particles following sonolysis. Each bar indicates the range of data.

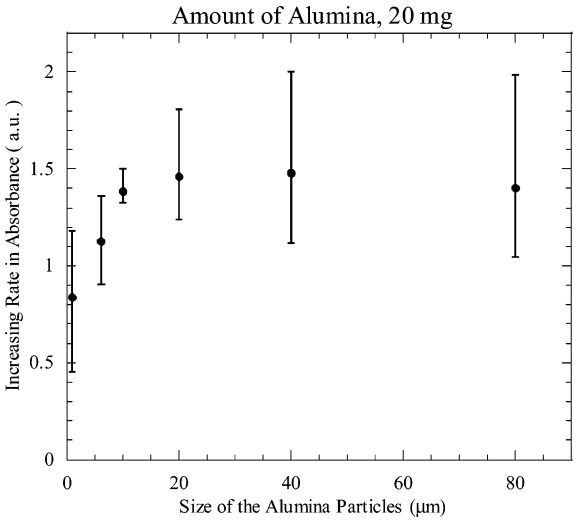

Figure 2. Particle-size dependence of the absorbance ratio of an aqueous KI solution with alumina particles (Al_2O_3) to that of a solution without particles following sonolysis. Each bar indicates the range of data.

Figure 2 shows the particle-size dependence of the absorbance ratio of an aqueous KI solution with alumina particles (Al_2O_3) to that of a solution without particles following sonolysis. In this case, the amount of particles was fixed to 20 mg as the highest ratio of the absorbance was obtained with this amount as observed in the previous case of particle dependence. The plotted data were averaged over three times. It can be observed that, in the range up to 10 μm, the absorbance ratio is low, while the ratio is stably high in the range of more than 10 μm. This result of low reaction yield at finer size of particles could not be explained from the concept that all of the nucleation sites on the surface of particles increase with the increased amount of particles, which results in an increase in the number of cavitation bubbles. Thus, the probable reason for the low

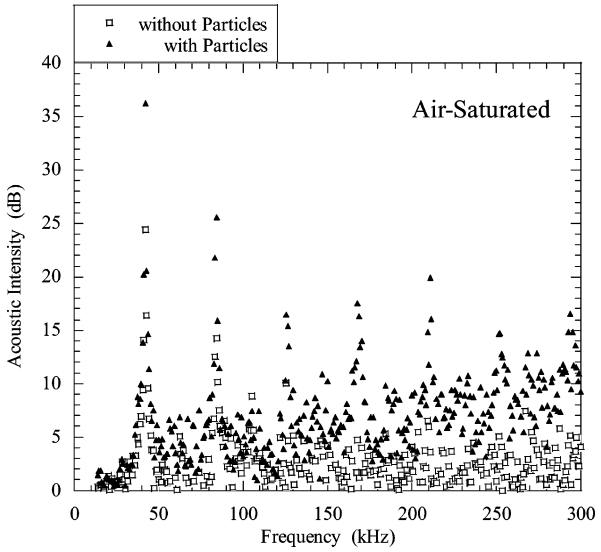

Figure 3. Cavitation noise spectra under sonication in cases with/without particles using air-saturated water.

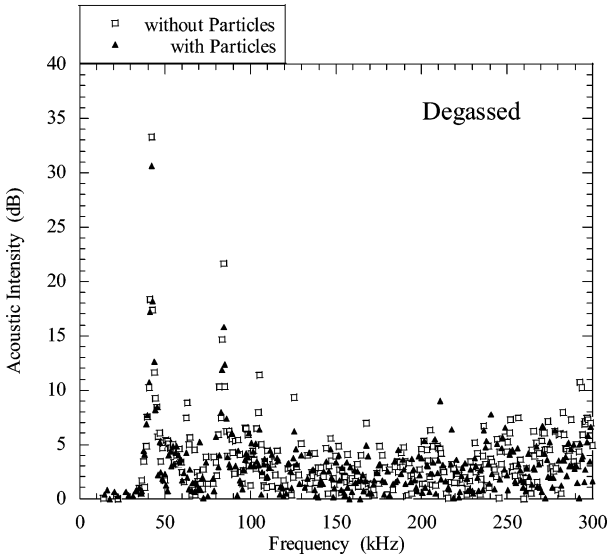

Figure 4. Cavitation noise spectra under sonication in cases with/without particles using degassed water.

reaction yield at finer size of particles may be due to that the small particles and the fluid that surround bubbles are in motion together, and the particles do not necessarily play a role of wall against bubbles to cause asymmetric collapse, leading to the generation of a large number of tiny bubbles.[4]

Figure 3 shows the cavitation noise spectra under sonication in cases with/without particles using air-saturated water. The plotted data are those averaged for 10 independent measurements, where the data are deducted in case of neither ultrasound nor particles. From this figure, the peaks at harmonics of ultrasonic frequency and superharmonics could be seen in the presence of particles, which are due to the nonlinear pulsation of cavitation bubbles. In the presence of particles, there is an increase in white noise as compared to that in the absence of particles. This result supports the fact that the appropriate addition of particles into a system of sonochemical reaction provides an increase in the number of active bubbles, leading to an enhancement in the yield. To evaluate the increase in the white noise, calculation was made for increasing ratio in area for the case in the presence of particles to that in the absence of particles. The calculated ratio was 3.26.

Figure 4 shows the cavitation noise spectra under sonication in cases with/without particles using degassed water. It has been found that the spectra in the presence of particles remained the same as that in the absence of particles. Under such degassed conditions, there could be little cavitation bubbles to cause white noise.

The ultrasonic power dissipated into a liquid is calculated by the following equation:

$$\text{power (W)} = (\mathrm{d}T/\mathrm{d}t)C_pM \qquad (1)$$

where $\mathrm{d}T/\mathrm{d}t$ is the temperature rise per second at time zero (K s^{-1}), C_p is the heat capacity of a liquid (J g^{-1}), and M is the mass of a liquid (g).[11,13,14] If a liquid is water, C_p is 4.2 J g^{-1}. It should be noted here that, when a large amount of cavitation bubbles are generated and which oscillate volumetrically in the liquid with sonication due to the large amount of dissolved gas, then the power in eq 1 comes mainly from the temperature rise due to the heat conducted from hot spot inside the collapsing bubbles to bulk liquid together with a friction between the liquid and the cavitation bubbles in volumetric oscillation. This power is different from that estimated by considering only the dissipation of a sound propagation in degassed liquid. Dissolved gas in a liquid is the origin of cavitation bubble for sonochemical reaction. Actually, a quantitative evaluation of sonochemical efficiency has been successfully performed using gas-saturated liquid prepared before sonication.[11] Accordingly, calorimetric study for sonochemical efficiency under gas-dissolved condition is effective based on the point of how much the cavitation bubbles could be generated.

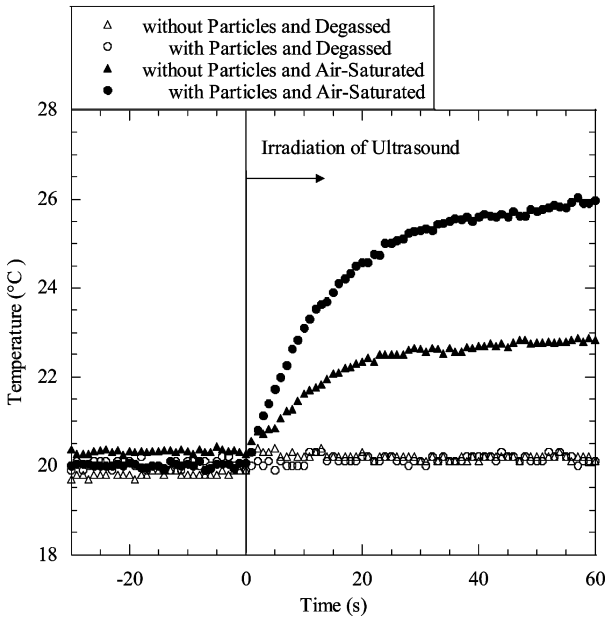

Figure 5. Comparison in the temporal variations of temperature between several combinations in the presence and absence of added particles, and degassed or air-saturated water.

Figure 5 shows the relationship in the temporal variations of temperature between several combinations of presence and absence of added particles, and degassed or air-saturated liquid. It has been observed that, just after starting the sonication, there were obvious rises in temperature for both cases of the air-saturated liquids as shown in Figure 5 (filled symbols). Calorimetric estimations of the power for this case using eq 1 provide us the wattage. The power was 1.7 W in the presence of particles, while it was 0.72 W in the absence of particles. Through the measurements of both the cavitation noise and the

temperature rise, we have confirmed that the appropriate addition of particles increases the number of oscillating bubbles active for sonochemical reaction.

4. Conclusion

The present investigation has shown that the addition of particles with appropriate amount and size results in an increase in the yield of sonochemical reaction. The acoustic noise together with the rise in the liquid temperature due to cavitation bubbles increase during such particle addition. This supports that the appropriate addition of particles increases the number of cavitation bubbles to enhance the yield in the sonochemical reaction.

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