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Laser-Light Scattering from a Multibubble System for Sonochemistry

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The oscillation of ultrasonic cavitation bubbles at various dissolved-air concentrations in a sonochemical reaction field is investigated experimentally by laser-light scattering. When a thin light sheet, finer than half the wavelength of sound, is introduced into the cavitation bubbles at an antinode of sound pressure, the scattered light intensity oscillates. The peak-to-trough light intensity is correlated with the number of bubbles that contribute to the sonochemical reaction. It is shown that as the dissolved air concentration is changed, the behavior of the spatial summation of the peak-to-trough intensity, determined by taking the degassing bubbles into account, is in good agreement with the behavior of the sonochemical reaction yield. Therefore, the present method of light scattering has proven to be a good cavitation-bubble detector for sonochemistry.

Irradiation of intense ultrasound into an aqueous solution generates cavitation bubbles. The subsequent violent collapse of multiple bubbles causes hot spots in the solution with temperatures of several thousand kelvin, pressures of about 1000 atm, and heating and cooling rates above 10^{10} K/s.[2−5] Under such extreme conditions, water dissociation takes place very easily, generating hydroxyl radicals that undergo various chemical reactions often referred to as sonochemical reactions.[2,6]

Analysis of the mechanism of cavitation-bubble dynamics is expected to lead to the achievement of high efficiency in cavitation-induced (sonochemical) reactions[7−10] and several experimental and theoretical studies on the behavior of cavitation bubbles characterized by the spatial distribution of the number and size of bubbles have been reported.[11−14] Lauterborn et al.[11] reviewed the bubble dynamics from a single bubble to multiple bubbles and showed that, in the case of multiple bubbles, the bubbles are confined to a spatial region by the action of primary and secondary Bjerknes forces, dependent on the applied acoustic amplitude.[12] Negishi measured the volumetric change in cavitation bubbles by light scattering and showed that multibubble sonoluminescence is generated at the time of collapse of the bubbles;[13] however, a relationship between the number of cavitation bubbles and sonochemical reaction yield was not investigated. Burdin et al.[14] investigated experimentally the size and volumetric concentration of acoustic cavitation bubbles with two laser techniques, laser diffraction, and phase Doppler interferometry. However, the oscillation of cavitation bubbles was not reported. As far as we know, there is as yet no published experimental report on the evaluation of the number of oscillating cavitation bubbles required for efficient sonochemical reactions.

The present report investigates, for the first time, multiple oscillating cavitation bubbles active for sonochemical reaction by light scattering, where an “active” bubble means a strongly oscillating bubble able to cause sonochemical reactions. When a thin light sheet, finer than half the wavelength of sound, is introduced into the cavitation bubbles at an antinode of sound pressure, the scattered light intensity oscillates. The waveform of the scattered light is a superposition of scattered light intensity from the scattering cross section of each bubble repeatedly expanding and contracting due to the acoustic cycle. The peak-to-trough light intensity, the difference between the maximum and minimum of the light intensity, corresponds to the relative number of bubbles that contribute to the sonochemical reaction. This is because the ambient radius for oscillating bubbles at the pressure antinode is restricted to a certain range due to shape instability[15,16] and the action of Bjerknes force[11,12] that expels bubbles larger than the resonant size from the antinode.

To evaluate the changes in the relative number of active bubbles, peak-to-trough intensity measurements were made of the scattered light from bubbles at around the pressure antinode in the ultrasonic standing-wave field for various dissolved air concentrations, since the number of cavitation bubbles is directly related to the concentration of the dissolved air.[17] Then, the yield of the sonochemical reaction for the liberation of iodine from an aqueous KI solution under ultrasound irradiation was measured for comparison with the results obtained by laser-light scattering. Since large degassing bubbles that do not undergo violent oscillations can pass through not only nodes but also antinodes on their way to the liquid surface, overestimation of the degassing bubbles for the peak-to-trough scattered light intensity measured at the antinode should be eliminated by deducting the intensity at the node from the intensity at the nearest antinode to provide the net intensity due to violently oscillating tiny bubbles effective for sonochemical reaction (Oscillation of scattered light intensity is observed even near pressure nodes because of the existence of progressive wave components.). Also, there are relatively fewer cavitation bubbles near the sound source compared with the number of bubbles near the liquid surface due to the action of the radiation force

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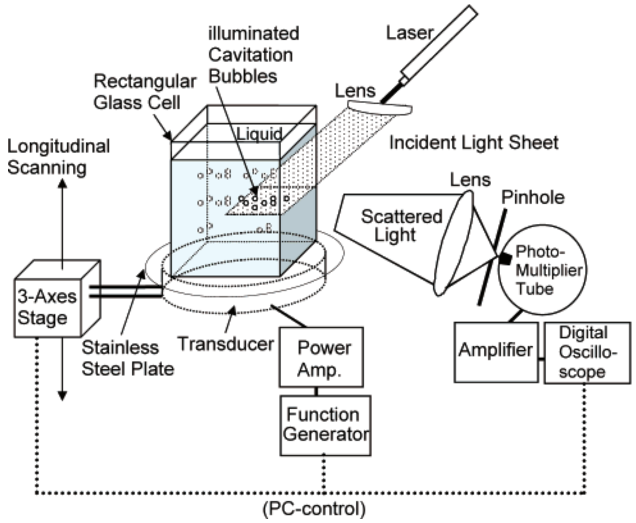

Figure 1. Experimental setup for laser-light scattering.

and cavitation-induced fluid motion. Hence, a spatial summation of peak-to-trough scattered light intensity in a reaction vessel is required, in contrast to the measurement of sonochemical reaction yield, which is averaged in the bulk liquid. Spatial summation of the difference in peak-to-trough values of scattered light intensity between antinodes and nodes over the range from the bottom of a vessel to the liquid surface corresponds to the relative total number of active cavitation bubbles (reaction sites) for sonochemistry. A change in the spatial summation can be related to a change in the yield of sonochemical reactions, as is estimated below.

Figure 1 shows the experimental apparatus for light scattering. A continuous wave sinusoidal signal of 142 kHz, generated by a function generator (NF Electronic Instruments, 1946), was amplified by a 55-dB power amplifier (ENI, 1140LA). The electric output was fed to a 50 mm diameter plane-type transducer (Honda Electronics) fixed to a stainless steel plate. A rectangular glass cell of 50 × 50 × 145 mm^3 internal dimensions was set above the transducer. The thickness of the glass cell was 5 mm. The cell contained 250 cm^3 of distilled water at a temperature of 20 °C. The air concentration of the distilled water was adjusted by air-bubbling. The concentration of dissolved oxygen (DO) in the distilled water served as an index of the amount of dissolved air. In the liquid, a standing wave was formed by the superposition of an incident wave from the transducer and a reflected wave from the air−liquid interface. A diode laser beam (NEOARK, 50 mW, 684 nm, 1 mm diameter), modified with a lens to a 0.5 mm thick sheet, was scanned from the cell bottom to the liquid surface by a three-axes stage (SIGMA KOUKI, LTS-50) in steps of 1.0 mm in the direction of sound propagation, and the intensity of the light scattered from the bubbles was measured with a photomultiplier tube (Hamamatsu Photonics H7732-10). The illuminated area was tetragonal and half of the plane was surrounded by the cell, one side of which was set close to the sound beam axis. The waveform of the scattered light was recorded with a digital oscilloscope (YOKOGAWA, DL1540C). Each set of data obtained was averaged over 32 scans. The ultrasonic power input to the cell was determined calorimetrically to be 17 W.

Measurements of the yield of the sonochemical reactions for the liberation of iodine from an aqueous KI solution were carried out under the same driving frequency. Ultrasonic irradiation into an aqueous KI solution causes oxidation of I^- ions to give I_2, which reacts with I^- to form I_3^- ions in the presence of excess I^- ions.[18,19] The absorbance was measured with a spectrophotometer (JASCO, V-530) within the range from 300 to 500 nm, including the absorbance of I_3^- at 352 nm.[20] For this purpose, 250 cm^3 of 0.1 M KI aqueous solutions with different DO concentrations were prepared and sonicated for 3 min. Five minutes after the end of the irradiation, the absorbance of the solution was measured. I_3^- is homogenized spatially in the cell by the mixing of the fluid induced by the bubble motion due to the radiation force. Therefore, a change in the sonochemical reaction yield of spatially homogeneous I_3^- should be compared with a change in the spatial summation of the peak-to-trough value of the scattered light intensity determined taking the contribution of degassing bubbles into account, as stated above.

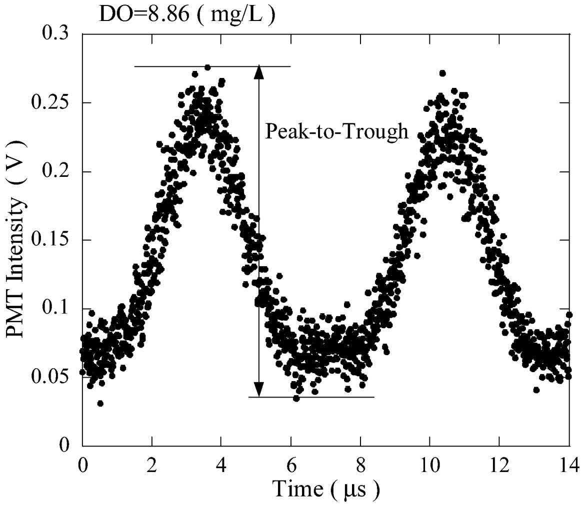

Figure 2. Example of measured waveform of scattered light from cavitation bubbles.

Figure 2 shows an example of a measured waveform of the intensity of scattered light from cavitation bubbles at 8.86 mg/L DO concentration, where the liquid is air-saturated. This figure confirms that the intensity oscillates with the same period, 7 μs, as that for applied ultrasound. To clarify the relationship between the spatial summations of the peak-to-trough intensity and sonochemical reaction yield, investigations were carried out for various DO concentrations.

Figure 3 shows a comparison of the DO-concentration dependence between the spatial summation of the difference in peak-to-trough scattered light intensity between antinodes and nodes, and the peak value of the I_3^- absorbance. It is notable that there is a sudden increase in the scattered light intensity at almost the same DO concentration (4.2 mg/L) for both, which implies that a cavitation and absorbance threshold occur together. The dependency at higher DO concentration is also similar between the two. The decrease in both the light intensity and absorbance at higher DO concentration may be due to a decrease in the acoustic amplitude as the sound is absorbed and scattered by the bubbles; that is, the number of little oscillating bubbles ineffective for sonochemical reactions increases relatively. It should be noted here that there is a probability to cause superoxide/hydroperoxyl radical leading to the sonochemical oxidation of iodide ions when sonolysis is conducted in the presence of dissolved oxygen[21] and further investigation is required.

Through the above investigation of scattered light from cavitation bubbles and a comparison with the sonochemical reaction yield, we conclude that the present method of light scattering has proven to be a good cavitation-bubble detector for sonochemistry. Another tool for cavitation noise measure-

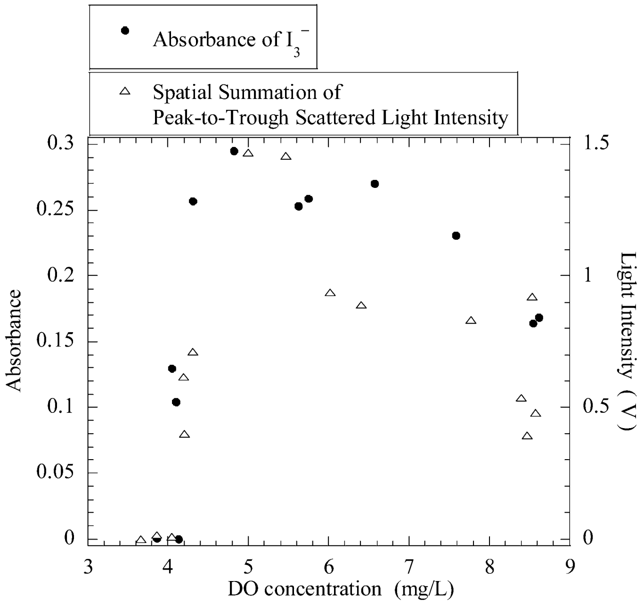

Figure 3. Comparison of DO-concentration dependence between the spatial summations of the difference in the antinode and node peak-to-trough values of scattered light intensity and the peak value of I_3^- absorbance. Open triangles represent the intensity summation, where the plotted intensity is the value at the intermediate DO concentration, determined from DO concentration measurements before and after irradiation. Filled circles represent the peak value of absorbance, where the intermediate DO concentration was used to plot the data, similar to the case of the scattered light-intensity measurement.

ment has been suggested by Segebarth et al.,[22,23] which studies the correlation between the width of the second harmonic and sonochemical activity. A detailed comparison between the present method of light scattering and the method of cavitation noise spectra, together with a study of the DO-concentration dependence of multibubble sonoluminescence will provide us with further information on cavitation bubbles active for sonochemistry. Also, obtaining a quantitative idea about the number of bubbles and light intensity/sonochemical yield has been left to a future study.

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