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Mechanism of Enhancement of Sonochemical-Reaction Efficiency by Pulsed Ultrasound

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The enhancement of sonochemical-reaction efficiency by pulsed ultrasound at 152 kHz has been studied experimentally through absorbance measurements of triiodide ions from sonochemical oxidation of potassium iodide at different liquid volumes to determine sonochemical efficiency defined by reacted molecules per input ultrasonic energy. The mechanism for enhancement of the reaction efficiency by pulsed ultrasound is discussed using captured images of sonochemiluminescence (SCL), and measured time-resolved signals of the SCL pulses and pressure amplitudes. The high sonochemical-reaction efficiency by pulsed ultrasound, compared with that by continuous-wave ultrasound, is attributed both to the residual pressure amplitude during the pulse-off time and to the spatial enlargement of active reaction sites.

Intense ultrasound radiated into a liquid creates collapsing cavitation bubbles,[1] which have uniqueness of high temperature, high atmospheric pressure, and rapid heating and cooling rates.[2] Some oxidants of hydroxyl radicals, hydrogen peroxide, ozone etc. are created inside the bubbles.[3] The oxidants react with chemicals such as luminol and emit light, called sonochemiluminescence (SCL).[4] Chemical reaction with acoustic bubbles is referred to as sonochemical reaction,[2,5] which is expected to be a useful tool for novel material synthesis,[6] environmental treatment,[7,8] biological application,[9] etc.

An irradiation of pulsed ultrasound is useful to obtain highly efficient sonochemical reaction.[10–12] Casadonte et al.[11] showed that both a high yield of H_2O_2 production and SCL patterns enlarged toward the side wall of the vessel were obtained using a modulated mode sonication, compared with those from a continuous-wave (CW) mode. Henglein et al.[12] suggested that the chemical yield is closely connected to the lifetime of the bubbles. As the pulse-off time becomes longer, smaller bubbles dissolve into the liquid more rapidly, because of the higher excess internal pressure $2\sigma/r$ (σ, surface energy; r, radius). However, the mechanism for the effective change of the spatial region in sonochemical reactions with a liquid volume under pulsed ultrasound has not been sufficiently investigated.

The effective region of sonochemical reaction is spatially restricted when using CW ultrasound, because many degassing bubbles[1] are created under such conditions of sonication. These degassing bubbles are ineffective for sonochemical reaction, due to their small volumetric oscillation, and they prevent the propagation of sound by absorption and scattering of the sound, which leads to a decrease in the sound pressure amplitude. As a result, the spatial region for those bubbles that expand and contract violently, leading to sonochemical reaction, is limited. Therefore, it is important to optimize the spatial distribution of cavitation bubbles and the sound field to accomplish high sonochemical efficiency in a large-scale container for industrial applications, and this can be effectively implemented using pulsed ultrasound. An appropriate pulse-off time that is specific to the ultrasound pulsing operation suppresses the generation of degassing bubbles formed by the coalescence of bubbles, thereby promoting a high amplitude of sound propagation that leads to the expansion and contraction of the bubbles. Therefore, the number of bubbles that are effective for sonochemical reaction is increased.

In this study, the chemical effects of pulsed ultrasound are investigated by absorbance measurements of triiodide ions from the sonochemical oxidation of potassium iodide[13] at different liquid volumes, to determine the sonochemical efficiency defined by reacted molecules per input ultrasonic energy. The mechanism of highly efficient sonochemical reaction by pulsed ultrasound is examined together with captured images of SCL and measured time-resolved signals of SCL and pressure amplitude.

In this experiment, a continuous or pulsed wave sinusoidal signal of 152 kHz is generated by a function generator (NF Electronic Instruments, 1942), and amplified by a power amplifier (ENI, 2100L, or Honda Electronics, L-400BM-L) to drive a Langevin-type transducer (Honda Electronics, o.d. 45 mm) attached to a transducer plate (2 mm thick, o.d. 100 mm). The transducer plate is located at the bottom of a slender liquid container made of stainless steel. The container is slender with a rectangular shaped inner volume ($100 \times 100 \times 1510$ mm^3) and has six observation windows. The container was filled with an aqueous solution of 0.1 M potassium iodide (Wako) prepared from distilled water, and the solution was saturated by air. Bubbling was performed during sonication at the corner of the container interior, in order not to disturb the sound field. The oxidation of I^- provides I_2, and I_3^- is produced by the reaction of I_2 and I^- in the presence of excess I^-.[13] The absorbance of I_3^- was measured with a spectrophotometer (Jasco, V-530) within the range 280−600 nm, including the peak at 352 nm.[14] The peak absorbance value was measured under different conditions of liquid volume and the way of sonication that was CW or pulsing operation. The liquid volume was varied from

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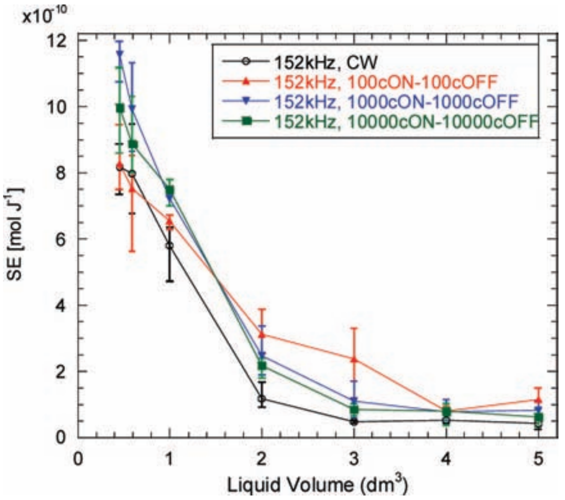

Figure 1. Dependence of sonochemical-reaction efficiency (SE) on the liquid volume.

0.45 to 5.00 dm^3, with a corresponding liquid height ranging from 44.0 to 477 mm. The liquid temperature inside the container was maintained at 25 ± 1 °C using a water circulation cooling jacket attached to the outside of the container. At each liquid volume, the ultrasonic power was estimated calorimetrically[13] using a thermocouple set at an intermediate position of the liquid volume. The calorimetrically determined ultrasonic power was 29 ± 4.5 W, and was relatively constant within the range of liquid volume used. The net ultrasound irradiation time was varied from 450 to 3600 s for both CW and pulsed ultrasonication, depending on the liquid volume. The pulsing operation condition was a repetition of n-acoustic cycles-ON and n-acoustic cycles-OFF (variable $n = 100$, 1000, or, 10000). From the measured absorbance of I_3^- and the ultrasonic power, the sonochemical-reaction efficiency (SE) was calculated by the following equation,[15]

$$SE = C_I/(Pt/V_I) \quad (1)$$

for CW and pulsed ultrasound at different n and different liquid volumes, where C_I denotes the I_3^- ion concentration in the 0.1 mol dm^{-3} KI solution, V_I is the solution volume, P is the ultrasonic power, and t is the net time of irradiation. Note that the ultrasonic power was calorimetrically determined at each liquid volume under CW ultrasound. The ultrasonic power for the pulsed mode was regarded as the same as that for CW if the net irradiation time between the CW and the pulsed modes was common.

Figure 1 shows the dependence of the sonochemical-reaction efficiency (SE) on the liquid volume. As the liquid volume increases, each SE value at 152 kHz decreases monotonically,[16] because the region that is greater than the cavitation threshold decreases as the liquid volume increases. A maximum SE of 1.2×10^{-9} mol J^{-1} was obtained for 1000 cycle ON−1000 cycle OFF at 152 kHz, which is 1.9 times higher than the reported maximum SE (6.4×10^{-10} mol J^{-1}) at 128.9 kHz CW from the literature.[15] The results reported in the literature[15] were obtained with operating parameters of ultrasonic frequency at 45.0, 128.9, 231.0, and 490.0 kHz, and at different liquid heights up to 700 mm. Compared with the reported maximum SE (6.4×10^{-10} mol J^{-1}) at 128.9 kHz CW ultrasound in a liquid volume of 0.585 dm^3 from the literature,[15] the SE (8.0×10^{-10} mol J^{-1}) obtained at 152 kHz CW and in a liquid volume of 0.587 dm^3 in the present experiment was higher.

With regard to the influence of volume change in the longitudinal direction (change in the height of the liquid) on the sonochemical-reaction yield, Henglein showed a periodic increase and decrease in the yield at an ultrasonic frequency of 10 kHz as the volume increased (height increase);[17] the periodicity has the successive maxima separated by half a wavelength of sound. This appears to be due to the sound field resonance sensitivity to the specific liquid height, especially at low frequency where the sound source is located at the bottom of the vessel. The magnitude of the maxima decreases monotonically as the liquid volume increases (height increases).

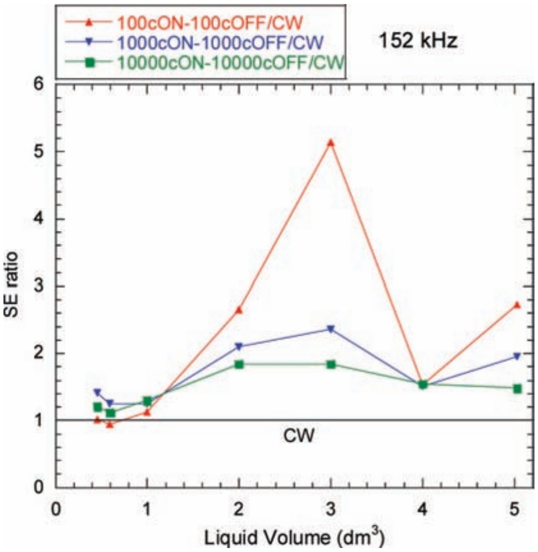

Figure 2. Liquid-volume dependence of the sonochemical-reaction efficiency (SE) ratio of pulsed ultrasound to continuous-wave (CW) ultrasound.

Figure 2 shows the liquid-volume dependence on the ratio of the pulsed ultrasound SE to the CW ultrasound SE, where most of the ratios are greater than 1. In this study, pulsing operation was found to be the most efficient compared with CW operation. It is remarkable that at 3 dm^3 and 100 cycle ON−100 cycle OFF, the ratio is the highest with an efficiency that is 5.1 times higher than that under CW operation. A sudden decrease in the ratio was observed for liquid volumes greater than 3 dm^3. Further investigation is required to clarify the sudden decrease; however, the origin of the high ratio obtained at 3 dm^3 is discussed below.

Figure 3 shows a comparison between photographic images of luminol-SCL at 3 dm^3 under different conditions of pulsed ultrasound. The SCL images were captured with a digital camera (Nikon, D70). Luminol (3-aminophthalhydrazide) reacts with OH radicals generated in the cavitation bubbles to yield aminophthalate anions and a blue fluorescence when intense ultrasound propagates through the luminol solution,[18] that is, the luminol exhibits SCL. A solution consisting of 0.33 M NaOH (Wako) and 1.9 mM luminol (Wako) was prepared using distilled water. The solution was saturated by air. The temperature of the solution in the container was set at 25 °C. From Figure 3, the region of luminescence, both around the center and near the liquid surface, becomes fainter in the order from (a) to (d). This tendency is consistent with the order of magnitude of the pulsed to CW SE ratio shown in Figure 2. As the pulse-ON time increases, the sound field during the pulse-ON time comes close to that during CW sonication. It is proposed that under CW sonication, sound propagation is prevented by the significant production of degassing bubbles, which results in a decrease in the sound pressure amplitude. Therefore, the luminescent region under CW sonication is narrow compared with that under pulsed mode sonication, where

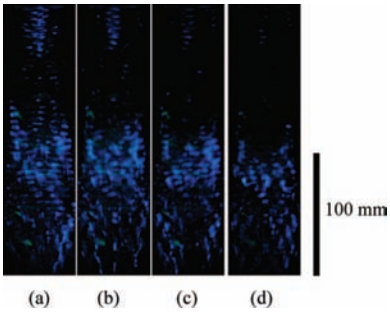

Figure 3. Comparison of luminol-sonochemiluminescence (SCL) photographic images for a liquid volume of 3 dm^3 under different conditions of pulsed ultrasound; pulsed ultrasound repetition of (a) 100 cycle ON−100 cycle OFF, (b) 1000 cycle ON−1000 cycle OFF, (c) 10000 cycle ON−10000 cycle OFF, and (d) CW ultrasound. Note that the exposure time for capturing the images was 3 min for (a), (b), and (c), and 1.5 min for (d). The exposure times were selected to equalize the net irradiation time between different conditions. Note that the top of each image corresponds to the liquid surface and the bottom corresponds to the position of 60 mm from the transducer plate.

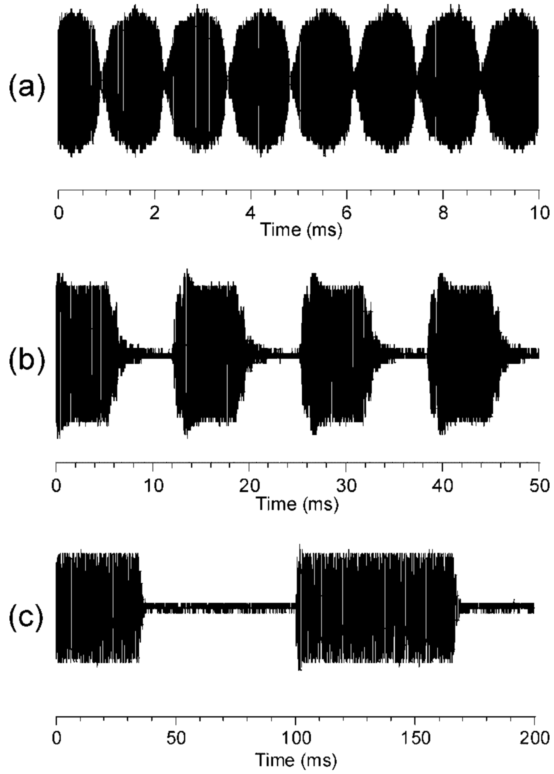

Figure 4. Measured waveforms of sound-pressure amplitude under different conditions of pulsed ultrasound; pulsed ultrasound repetition of (a) 100 cycle ON−100 cycle OFF, (b) 1000 cycle ON−1000 cycle OFF, and (c) 10000 cycle ON−10000 cycle OFF. Note that each vertical axis is an arbitrary unit and each time scale is different.

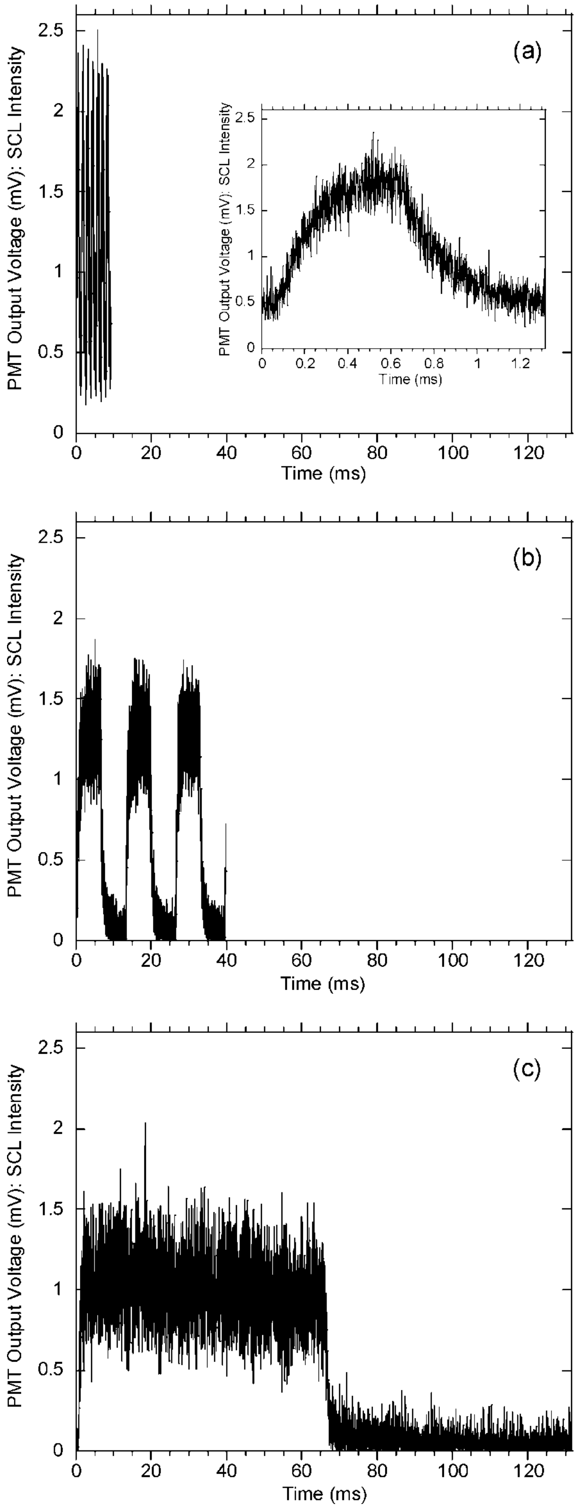

Figure 5. Measured waveforms of SCL intensity under different condition of pulsed ultrasound; pulsed ultrasound repetition of (a) 100 cycle ON−100 cycle OFF for seven times, (b) 1000 cycle ON−1000 cycle OFF for three times, and (c) 10000 cycle ON−10000 cycle OFF for one time. The inset of (a) shows a magnified view of one time.

the influence of degassing bubbles is suppressed. It was found that the high efficiency in the sonochemical reaction comes partly from spatial enlargement of the active region. It is noteworthy that the active region can be extended in the longitudinal direction using pulsed ultrasound.

Figure 4 shows measured waveforms of sound-pressure amplitude under different conditions of pulsed ultrasound. The measurement was performed at a pressure antinode nearest to the liquid surface when the liquid volume was 3 dm^3, using a hydrophone (Brüel and Kjær, 8103) and a digital oscilloscope (Yokogawa, DL1540C). Figure 4a shows that the acoustic amplitude increases and decreases periodically but barely reaches zero. The residual acoustic amplitude is effective for reuse of the seed bubbles for pulsation.[12] From Figure 4b,c, a contrast in the rest time is apparent; as the rest time proceeds, tiny bubbles dissolve in the liquid and the number of bubbles for effective sonochemical reaction decreases.[19]

Figure 5 shows measured waveforms of the SCL intensity at an antinode nearest to the liquid surface under conditions of pulsed ultrasound for the luminol solution prepared similarly to that in Figure 3. SCL was detected using a photomultiplier sensor (Hamamatsu Photonics, H7732-10), and the waveform was observed using a digital oscilloscope. The time-averaged intensity of SCL was compared between Figure 5a–c. A magnitude of intensity in the order of (a) > (b) > (c) was obtained. This is consistent with the order of magnitude found for the SE ratio shown in Figure 2. The inset of Figure 5a (100 cycle ON–100 cycle OFF) shows that the SCL intensity has a long tail relative to the pulse-off time. This is attributed to the sound pressure amplitude that barely reaches zero during the rest time, as seen in Figure 4a. In Figure 5b (1000 cycle ON–1000 cycle OFF) and Figure 5c (10000 cycle ON–10000 cycle OFF), the intensity decays and reaches zero during the rest time, according to the pressure variation shown in Figure 4b,c. Dekerckheer et al.[20] studied SCL pulses at different pulse-lengths and on/off pulse ratios, and results of SCL pulse similar to those shown in Figure 5 were reported. Ashokkumar et al.[21] showed that a sonoluminescence pulse different from that of SCL develops, and the intensity plateaus with a pulse length corresponding to the change in the waveform of the pressure amplitude. However, so far, a mechanism for the enhancement of SE by pulsed ultrasound has not been identified from both the measured pressure amplitude and the SCL pulse. The present results may be evidence that the population of sonochemically active bubbles is closely related with the residual acoustic pressure. The residual pressure amplitude maintains a certain number of pulsating bubbles due to the suppression of dissolution.

Thus, high SE by pulsed ultrasound, compared with that by CW ultrasound, is attributed both to the residual pressure amplitude during the pulse-off time and to the spatial enlargement of active reaction sites. The effect of spatial enlargement is also obtained using a partially degassed solution, even under CW ultrasound. The authors have previously studied the sonochemical oxidation of potassium iodide at different dissolved-gas concentrations[22] and showed that the relative SE at intermediate concentrations is at most 2 times higher compared with that at saturation, and the oxidation could not be observed for a completely degassed solution. Accordingly, it is proposed that the effect of residual pressure amplitude is superior to that of spatial enlargement.

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