Enhancement of Sonochemical Reaction Rate by Addition of Micrometer-Sized Air Bubbles

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The sonochemical reaction rate has been enhanced by the introduction of tiny air bubbles. The bubbles including micrometer-sized ones are produced by method of atomization and are introduced into aqueous luminol solution under 141-kHz sonication in order to investigate the enhancement of sonochemical reaction rate by introduction of tiny bubbles through the intensity measurement of sonochemiluminescence (SCL). It is shown that the introduction of tiny bubbles under sonication accomplishes the large SCL intensity compared to the cases of sonication only and liquid flow under sonication. It is also shown that it is important to adjust the configuration of tiny-bubble addition to the sound field. Through the investigations on the intensity and the spatial pattern of luminol−SCL, it has been clarified that tiny bubbles added into the sonicated liquid not only cause the liquid flow but also increase the number of collapsing bubbles active for sonochemical reaction. It is also shown that the tiny-bubble addition enhances the reaction rate of KI oxidation under sonication. Therefore, the present method of introduction of tiny bubbles is effective for enhancement of sonochemical reaction rate.

1. Introduction

Propagation of an ultrasonic wave in liquid generates cavitation bubbles when the acoustic pressure amplitude is more than the cavitation threshold.[1] The cavitation bubble repeats expansion and contraction according to the acoustic cycle. If the pressure amplitude is above the cavitation threshold, the bubble collapses rapidly and provides extreme condition of several thousands of Kelvins, several hundred atmospheric pressure, and heating and cooling rates greater than 10^9 K/s[2]. The collapsing cavitation bubble produces some oxidants of hydroxyl radical, oxygen atom, hydrogen peroxide, etc., by decomposition of water if the liquid is water.[2,3] Chemical reaction with these oxidants from acoustic cavitation bubble is called sonochemical reaction.[2−4] One of the important points for accomplishment of high efficiency[5] in the reaction is how one increases the number of collapsing cavitation bubbles.

Tiny gas bubbles including micrometer-sized ones can be produced mixing compressed gas with liquid by method of atomization.[6,7] However, to our knowledge, there is no attempt to enhance sonochemical reaction rate by the addition of tiny bubbles using the atomization method.

In this study, an effect of bubble addition on the sonochemical reaction rate in a liquid irradiated by an ultrasound is investigated through measurements of sonochemiluminescence (SCL) intensity related closely with the amount of oxidants from the bubbles in a bulk-liquid region as well as capturing images of the luminescent spatial patterns. An influence of direction of tiny-bubble addition on intensity of SCL is studied. An effect of tiny-bubble addition and liquid flow on reaction rate of iodine liberation under sonication is investigated.

Since it is known that a bubble in a range from almost 1 to 10 μm in ambient size is effective for sonochemical reaction due to its large and violent compression of bubble,[8] an addition of tiny bubbles into the sound field has a probability to enhance the sonochemical reaction rate. It is noted here that the appropriate size is dependent on the acoustic pressure.

As for ultrasonic frequency, it is necessary to select the frequency between 100 and 600 kHz where the ultrasound driven within this frequency range is desirable for effective sonochemical reactions,[9,10] which has been confirmed experimentally.

Also, a fluid flow in a vessel has a probability to enhance the sonochemical reaction rate.[11] The fluid flow associated with tiny bubble addition is expected to enhance the sonochemical reaction rate.

When the tiny bubbles created in the above manner is introduced into a standing-wave field in a liquid, it is desirable that the tiny bubbles is added by appropriate amounts from the side near a sound source in the direction perpendicular to sound beam axis. This is because high acoustic amplitude near the sound source is useful.

A control of dissolved gas concentration in a liquid is important. It has been reported that saturation of dissolved gas does not necessarily good to effective sonochemical reaction.[12] Reduction in the concentration decreases the number of bubbles which suppresses the decrease in acoustic amplitude caused by absorption and scattering of sound due to bubbles during the propagation. Under the appropriately reduced concentration, it is possible to cause more bubbles to oscillate violently and a creation of more amount of oxidants is expected.

Thus, it is expected that the addition of tiny bubbles promotes sonochemical reaction in a sonicated liquid that has relatively low concentration of dissolved gas.

2. Experimental Section

Figure 1 shows the experimental apparatus. In the experiment, a continuous-wave sinusoidal signal of 141 kHz, generated by a function generator (NF Electronic Instruments, 1946), was amplified by a 55-dB power amplifier (ENI, 1140 LA) to drive a transducer of Langevin type (Honda Electronics, 45 mm in diameter). The calorimetric power was 30 W in a glass vessel of 150 × 150 × 170 mm^3 dimensions filled with 3.1 L luminol

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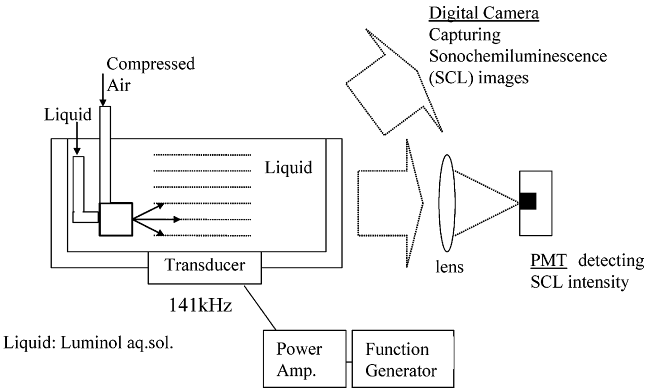

Figure 1. Experimental apparatus.

(3-aminophthalhydrazide) aqueous solution, where the solution prepared by mixture of 12.4 mL of 250 mM $NaCO_3$ 2.5 mM luminol and water. Luminol reacts with OH radicals generated in the cavitation bubbles to give aminophthalate anions and a blue fluorescence when the luminol solution is irradiated by intense ultrasound.[13] This is the luminol SCL. A gas dissolved in the solution was air. With adjustment of the concentration of dissolved air, the concentration was decreased by appropriate degassing under the ambient-pressure reduction with a vacuum pump as stirring. The concentration of dissolved oxygen (DO) in the liquid served as an index of the amount of dissolved air.

The tiny air bubbles produced by mixing compressed air (flow rate of air: 2.4 L/min) and liquid (flow rate of liquid: 188 mL/min) were introduced into aqueous luminol solution under 141-kHz sonication, where the tiny bubbles spouted from 0.6-mm hole nozzle of aerator (handcrafted) into the solution using both the pumps of air and liquid (air pump, AS ONE, LMP100; liquid pump, Cole-Parmer, 7553-70). In a chamber provided inside the aerator, the liquid collides and mixes with the compressed gas.[6,7] The gas inside the liquid provides the turbulence to the surrounding liquid with deformation of gas−liquid surface. The deformation develops over all the liquid. Finally, the liquid breaks to form a liquid drop by a coagulation of the broken liquid while the gas comes into tiny bubbles. The size distribution of the tiny bubbles added was measured using a particle sizer (AEROTRAC SPR, 7340) in absence of sonication. The temperature of the solution in the vessel was set at 27.5 °C.

The SCL image was captured with digital camera (Nikon, D70) and the intensity was measured using a photomultiplier tube (Hamamatsu Photonics, R928) in the presence or absence of the addition of liquid flow and micrometer-sized air bubbles under the several concentrations of dissolved air. A converging lens was set between the vessel and the photomultiplier tube to ensure that all the luminescent positions were detected. The concentration of dissolved oxygen was measured as a value in proportion to the concentration of dissolved air.

Iodine liberation was performed under the sonication in the presence or absence of the addition of liquid flow and micrometer-sized air bubbles in a manner similar to the above. Ultrasonic irradiation into an aqueous KI solution results in the oxidation of I^- ions to give I_2, and I_2 reacts with I^- to form I_3^- ions in the presence of excess I^- ions,[9,14] where the oxidation of iodide is attributed to the action of OH radicals in the cavitation bubbles which reach the liquid phase

$$H_2O \rightarrow H + OH \qquad (1)$$

$$OH + I^- \rightarrow OH^- + I \qquad (2)$$

$$2I + I^- \rightarrow I_3^- \qquad (3)$$

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. It has been confirmed that in absence of sonication the absorbance stays the background level when the tiny bubble is added.

Experimental procedure for KI oxidation by sonication under particles addition is as follows; 3.1 L aqueous KI solution (0.1 mol dm^{-3}) was bubbled by air for 30 min before sonication. The dissolved oxygen content in the solution before sonication was that for air saturation. During sonication, the bubbling was also performed at the position far from the sound field in order to reduce an influence of degassing with time. The duration of sonication was 30 min in each case.

3. Results and Discussion

3.1. Size Distribution of Added Tiny Bubbles. Figure 2 shows the size distribution of tiny bubbles from air-assist atomizer where the distribution has been measured under no sonication. It is found that there are the bubbles of which size is in a range of several micrometers. On the basis of the analogy to the bubble size for accomplishing large ratio in expansion and compression of a bubble in the literature,[8] the bubble size from 1 μm up to around 20 μm is active at 140 kHz close to the driving frequency (141 kHz) of the present study, although the state of pulsation is unstable and transient at around 10−20 μm. It is reasonable to assume that the bubbles from air-assist atomizer have a potential to contribute to sonochemical reaction.

3.2. Change of SCL Spatial Patterns due to the Addition of Liquid Flow and Tiny Bubbles. Figure 3 shows the photographs of SCL taken with a digital camera at three conditions of irradiation of ultrasound only, ultrasound under the addition of fluid flow, and ultrasound under the addition of tiny bubbles at near air-saturation together with the photograph of configuration. In the image of configuration, the vibrating plate set on the transducer is located at the bottom and liquid surface is on the upper end. It has been confirmed that at the case of ultrasound irradiation with addition of fluid flow the pattern of bright stripes is marked compared with the pattern at ultrasound only. It is noteworthy that the shape of bright SCL in (3) of Figure 3 is related closely with that of bubbly blowing flow

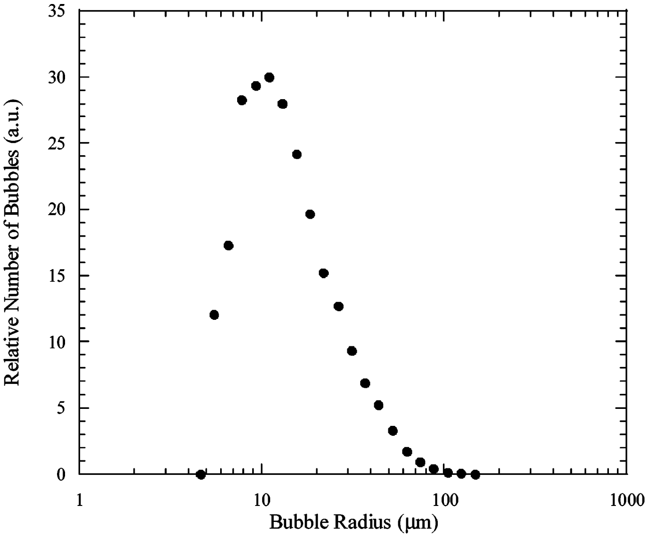

Figure 2. Measured size distribution of bubbles from air-assist atomizer.

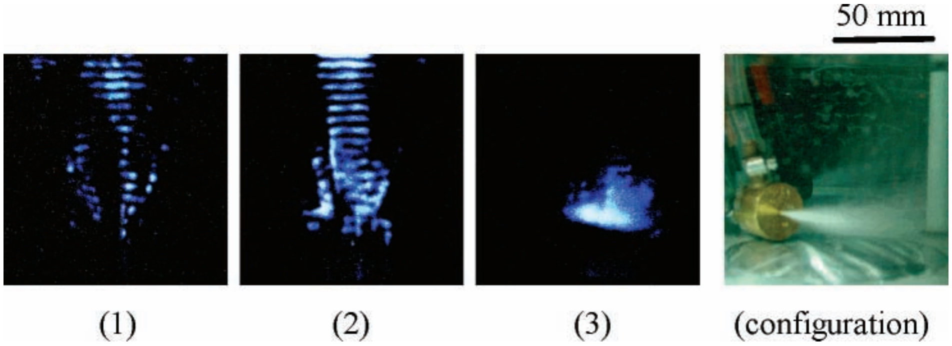

Figure 3. Photographs of SCL at three conditions of (1) sonication only, (2) sonication with the addition of fluid flow, and (3) sonication with the addition of tiny air bubbles at near saturation of dissolved air together with the photograph of configuration.

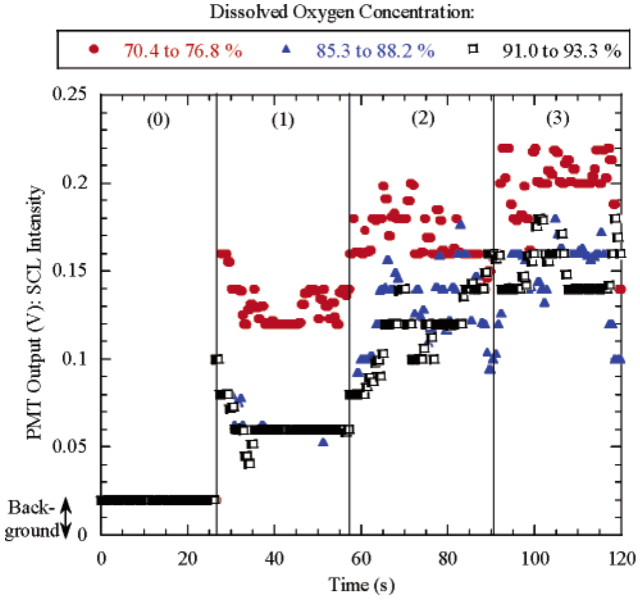

Figure 4. Time course of SCL intensity measured changing the conditions when each condition (0−3) was maintained during around 30 s: (0) silent, (1) sonication only, (2) sonication with the addition of fluid flow, and (3) sonication with the addition of tiny bubbles. Filled circles are the case of the dissolved oxygen concentration changed from 70.4 to 76.8% before and after sonication, filled triangles for 85.3−88.2%, and open squares for 91.0−93.3%. Note that the configuration when the tiny-bubble is added is along with a manner similar to Figure 1.

appeared in the configuration. It is remarkable that tiny bubbles added into the sonicated liquid directly result in an increase in the number of collapsing bubbles active for sonochemical reaction. It is seen in (3) of Figure 3 that transverse stripes of the luminescence due to standing wave on the upper side against the region of tiny bubbles added almost disappear. This implies that most of sound energy effective for sonochemical reaction is consumed by the tiny bubbles. As the region of tiny bubbles added is quite active for sonochemical reaction, the addition of tiny bubbles is promising for enhancement of sonochemical reaction rate.

3.3. Change of SCL Intensity Due to the Addition of Liquid Flow and Tiny Bubbles. Figure 4 shows the intensity measured changing the conditions as time proceeds. An increasing ratio of the intensity due to the different conditions of liquid flow, the addition of tiny bubbles, and the concentrations of dissolved air was defined against the intensity with sonication only. The ratio was calculated using the average data for each case in Figure 4. Note that there is no overlap between the concentrations of dissolved oxygen and it is meaningful to evaluate an effect of tiny bubble addition at the different concentration.

Table 1 shows the results at various conditions, those are normalized by the value obtained in the case of sonication only at around air saturation (91.0−93.3%). It is shown that an efficient reaction is obtained 2.7 times higher in the case of low concentration of dissolved air under sonication compared with the near-saturated case. Generally, the cavitation bubbles can be generated easily at higher concentration of dissolved gas as more. However, an excess amount of bubbles disturbs the propagation of ultrasound. The high efficiency as described in the present paper is obtained when under intense ultrasound the concentration of dissolved gas is set relatively low.

It is shown that a reaction rate 3.6 times higher is obtained for the combination of liquid flow and the low concentration of dissolved air (70.4−76.8%) under sonication in comparison with the case of sonication only. Fluid flow provides an effect of suppressing interbubble coalescence to keep the distance between bubbles. This flow also transports large-sized bubbles expelled from antinodes due to Bjerknes force back to the antinodes,[15] and they work in the sonochemical reaction. At this time, the number of bubbles generating high temperature and high pressure increases to enhance the sonochemical reaction rate.

It is shown that a reaction rate 4.3 times higher, the highest in the present attempts, is obtained for the combination of the addition of tiny bubbles and the low concentration of dissolved air (70.4−76.8%) under sonication in comparison with the case of sonication only.

Thus, the addition of tiny bubbles enhances sonochemical reaction rate. Note that, similarly to the effect of liquid flow, the drag motion of bubbles against the surrounding liquid causes a turbulent flow and may enhance the sonochemical reaction rate.

3.4. Influence of Direction of Tiny-Bubble Addition on Intensity of SCL. In this section, an influence of direction of tiny bubble addition on intensity of SCL is investigated. Addition of tiny air bubbles toward the vessel wall under sonication at around air saturation is attempted during sonication. The tiny bubbles migrate back to the sound field above the transducer. However, the density of the number of tiny bubbles there is quite lower than that in the case of Figure 4 (3). Figure 5 shows the time course of SCL intensity measured in the presence or absence of addition of tiny air bubbles. Compared with the results with addition of tiny bubbles in Figure 4 (3) (the right column in Table 1), there was a quite little enhancement of less than 10% by tiny-bubble addition determined from the time-averaged data. It is hard to enhance sonochemical reaction rate without fluid flow to transport the bubbles toward the sound field as in the above. To distribute the tiny bubbles throughout

TABLE 1: Increasing Ratio of SCL Intensity against the Intensity at Sonication Only at around Air Saturation (Marked with Asterisk) Calculated Using the Average Data for Each Case in Figure 4

dissolved oxygen concentration before and after intensity measurement (%)	increasing ratio of SCL intensity		
	(1) Figure 4 sonicated only	(2) Figure 4 sonicated; addition of liquid flow; flow rate of liquid, 262 mL/min	(3) Figure 4 sonicated; addition of liquid flow; flow rate of liquid, 188 mL/min; addition of air bubbles, flow rate of air, 2.4 L/min
70.4−76.8	2.7	3.6	4.3
85.3−88.2	1.1	2.5	3.1
91.0−93.3	1.0*	2.3	3.1

the system, liquid flow as well as stirring may be effective to obtain more enhancements.

Figure 6 shows the time course of SCL intensity measured in the presence or absence of addition of tiny air bubbles in the vertical direction under sonication at around air saturation. By tiny-bubble addition the intensity was apparently lower than that in case of sonication only. In the direction of tiny-bubble addition, due to the friction against the liquid the speed of motion of tiny bubbles rapidly decreases coalescing to each other to create large bubbles as the bubbles are blown from the nozzle toward the transducer. Since the large-sized bubbles scatter the sound, the tiny bubbles those are high in the number density near the nozzle do not accept a high amplitude of sound pressure and cannot contribute to sonochemical reaction effectively. It is seen that the low intensity of SCL at the bubble addition at the initial sonication becomes high and constant as time proceeds. This may be because a period is required for tiny bubbles to migrate near the transducer.

The configuration of bubble introduction as shown in Figures 1 and 3 is preferable because the above layer of large-sized bubbles is thinner in the direction perpendicular to that of bubble introduction and the sound can penetrate into the tiny-bubble region leading to the sonochemical reaction. Accordingly, one could obtain the enhancement of sonochemical reaction rate in the case of bubble addition in Figure 4 and Table 1. To obtain large number of pulsating bubbles for effective sonochemical reaction, it is desirable to transport a lot of tiny bubbles into a region of high-pressure amplitude. Fluid flow is necessary to transport the bubbles. Micrometer-sized bubbles are preferable for violent volumetric oscillation. This violent oscillation leads to extreme condition of high pressure and temperature inside the bubbles those provide oxidants.

3.5. Effect of Tiny-Bubble Addition and Liquid Flow on Reaction Rate of Iodine Liberation under Sonication. In this section, an effect of tiny-bubble addition and liquid flow on reaction rate of iodine liberation under sonication is investigated at air saturation. Figure 7 shows the measured curves of I_3^- absorbance at different conditions. In both cases of tiny-bubble addition and liquid flow addition, one could obtain the absorbance peaks higher than that at sonication only, where the absorbance was 0.06 at bubble addition under sonication, 0.06 at liquid flow addition under sonication, and 0.04 at sonication only (these values were rounded off to two decimal places). It seems in the figure that the effect of micrometer-sized bubbles on the absorbance of I_3^- is very tiny as compared to the effect of liquid flow. A ratio in the absorbance at tiny-bubble addition against that at liquid flow addition was then nearly equal to 1, while the ratio of SCL with luminol at around air saturation was high, that is, (0.06/0.06) vs (3.1/2.3). The difference between the two “monitors”, namely, luminol chemiluminescence and iodide oxidation, can be explained based on the surface activity of luminol. Since luminol is surface active, it adsorbs to the bubble interface and “traps” more OH radicals. Iodide is not surface active and reacts with OH radicals that escape into the

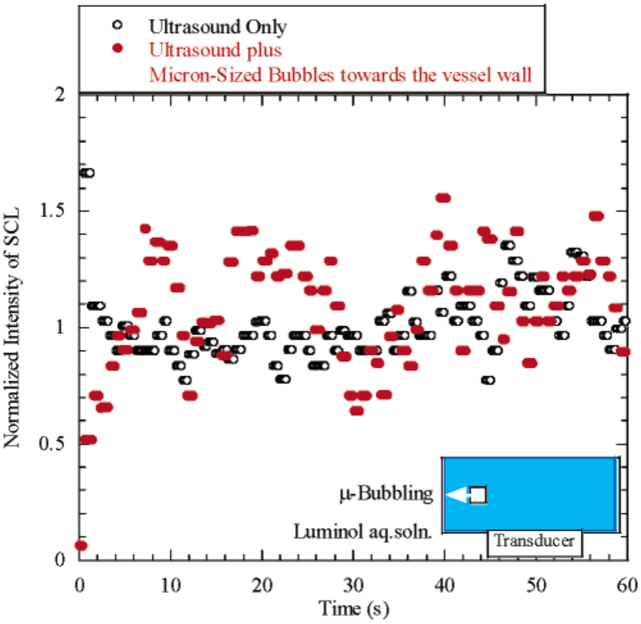

Figure 5. Time course of SCL intensity measured in the presence or absence of addition of tiny air bubbles toward the vessel wall under sonication at around air saturation. Note that the intensity is normalized by the intensity averaged over 0−60 s in each case. The inset inside the figure shows the configuration of the tiny-bubble addition.

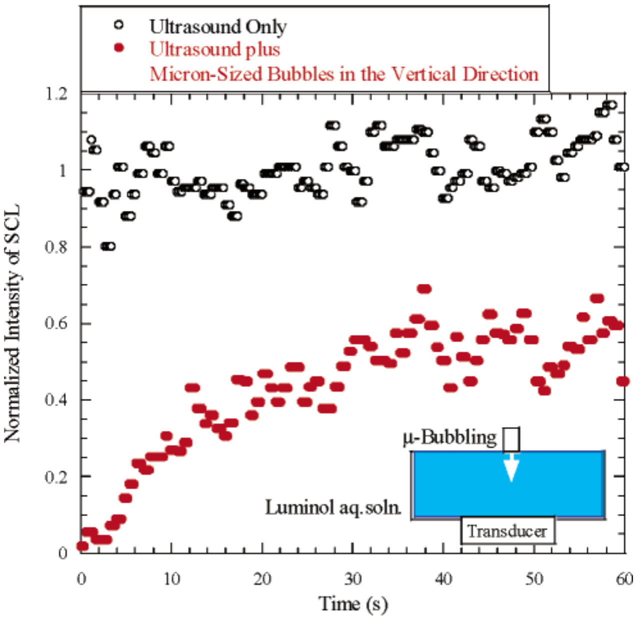

Figure 6. Time course of SCL intensity measured in the presence or absence of addition of tiny air bubbles in the vertical direction under sonication at around air saturation. Note that the intensity is normalized by the intensity averaged over 0−60 s in each case. The inset inside the figure shows the configuration of the tiny-bubble addition.

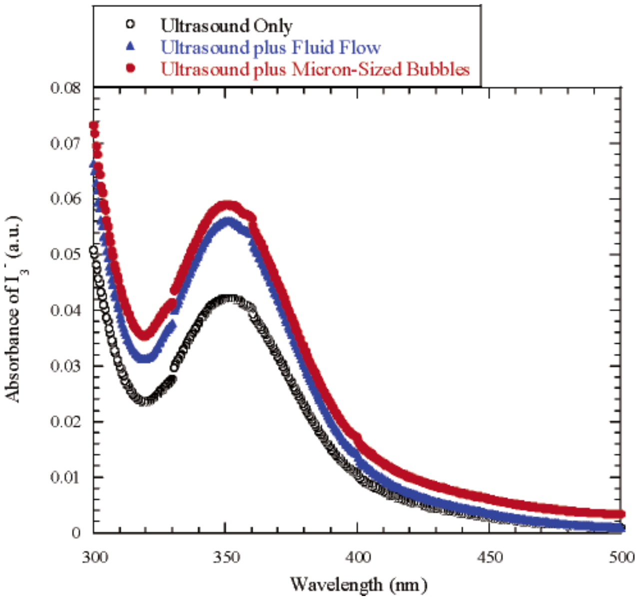

Figure 7. Absorbance of I_3^- measured in the presence or absence of addition of fluid flow and tiny air bubbles under sonication at around air saturation. Note that the configuration when the tiny bubble is added is along with a manner similar to Figure 1.

bulk solution. On the basis of this argument, luminol is a better indicator (monitor) of OH activity. Note that in case of iodine liberation under air the aqueous solution becomes acid to create HNO_2 as time of sonication proceeds, and HNO_2 consumes oxidants from cavitation bubbles to reduce the rate of I_3^-.[16] The influence by HNO_2 does not happen at luminol solution because the solution is usually adjusted to alkaline condition.

4. Conclusion

In conclusion, sonochemical reaction rate is enhanced by the addition of tiny bubbles and liquid flow, and the operation under the reduced amount of dissolved gas is more effective especially at the bubble addition. It has been found that it is important to adjust the configuration of tiny-bubble addition to the sound field. Through the investigations on the intensity and the spatial pattern of luminol−SCL, it has been clarified that tiny bubbles added into the sonicated liquid directly connect to an increase in the number of collapsing bubbles active for sonochemical reaction.

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