Influence of Surface Active Solute on Ultrasonic Waveform Distortion in Liquid Containing Air Bubbles

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The influence of sodium dodecyl sulfate (SDS) on waveform distortion of 141 kHz ultrasonic standing waves in liquids containing air bubbles was investigated for various transducer powers. Fast Fourier transform (FFT) operations were performed on the pressure waveform to obtain the harmonic components. In addition, the intensity of sonoluminescence (SL) was measured as a function of the power. Waveform distortion was observed for water at high applied power, with the curve exhibiting a steeper gradient for positive pressures and a broadened minimum for negative pressures. This was in reasonable agreement with theoretical studies reported in the literature. Much less distortion was found for a 1 mM SDS solution as the applied power was increased than for water or a 10 mM SDS solution. This may be attributed to a lower population of large coalesced bubbles in the 1 mM solution due to electrostatic repulsion, leading to damping of the sound energy and little cavitation noise because of viscous resistance to bubble radial motion in addition to adsorption and desorption of surfactant molecules at the bubble–liquid interface. For 10 mM SDS, the power threshold for the harmonic components was lower than that for the SL. In this case, it appears that there is a range of applied powers where most bubbles are stable and cannot collapse. The influence of the addition of an electrolyte and a nonionic surfactant was also investigated.

1. Introduction

Irradiation of a liquid with intense ultrasound creates cavitation bubbles,[1] which expand and contract repeatedly due to pressure variations caused by the ultrasound, and collapse rapidly above a certain threshold pressure amplitude. Extreme conditions exist inside the bubbles, including temperatures of several thousand kelvin, pressures of several hundred atmospheres, and heating and cooling rates greater than 10^9 K/s.[2] Inside such bubbles, water is easily decomposed and oxidants such as hydroxyl radicals, hydrogen peroxide, and ozone are created.[3] At the interface of the bubbles, these oxidants react with chemicals such as luminol, and light is emitted in a process known as sonochemiluminescence (SCL).[4] In addition, a process called sonoluminescence (SL) causes light to be emitted from the interior of collapsing cavitation bubbles.[4] Chemical reactions involving acoustic bubbles are referred to as sonochemical reactions,[2,5] and understanding their mechanism involves analysis of the sound field containing cavitation bubbles.

It is expected that the pressure waveform is distorted in a sound field containing bubbles. The bubbles can absorb the sound energy and transform it to a pulsating motion. According to several theoretical studies, the acoustic emission from pulsating bubbles is responsible for the distortion of the waveform. Zabolotskaya and Soluyan[6] first predicted analytically that a pulsating air bubble in water emits spherical waves with higher harmonic components if the bubble executes forced oscillations under the action of a harmonically alternating pressure. From this point of view, a pulsating bubble acts as a multifrequency sound source. As Caflisch et al.[7] and Miksis and Ting[8] have pointed out, an equation based on the mass conservation laws plus an additional term related to the bubble

radius and the number of bubbles can be used to describe the distortion of the pressure waveform propagating in a bubbly liquid. Since an incident wave is affected by cavitation noise from the pulsating bubbles, the pressure waveform becomes distorted.

To the best of our knowledge, there has been only one theoretical study by Vanhille and Campos-Pozuelo[9] on the distortion of pressure waveforms in a standing wave which contains bubbles. However, that study dealt only with the pressure waveform in an air–water system and not with a system containing any surface active solutes. Surface active solutes such as sodium dodecyl sulfate (SDS) can result in a uniform distribution of active bubbles throughout the sound field,[10] leading to the effective use of the entire vessel for high efficiency sonochemical reactions.

In this study, the influence of the addition of SDS on the sound-pressure waveform propagating through a layer of 141 kHz ultrasonic standing wave in a bubble-containing liquid was investigated by varying the applied power to the ultrasonic transducer. Fast Fourier transform (FFT) operations were carried out on the pressure waveform to obtain the harmonic components. The SL intensity was measured as a function of the applied power. The influence of the addition of an electrolyte (0.1 M NaCl) into a solution containing a low SDS concentration was also investigated. In addition, the behavior of solutions containing a nonionic surfactant (1 or 10 mM polysorbate20) was studied.

Note that the waveform distortion described here is different from that which occurs with finite amplitude due to nonlinearity of a medium which contains no bubbles.[11,12] In this mechanism, the instantaneous local sound velocity increases as the degree of compression (the instantaneous local density) increases. Thus, a portion of an acoustic wave which has a larger instantaneous local particle velocity propagates faster than the remainder of

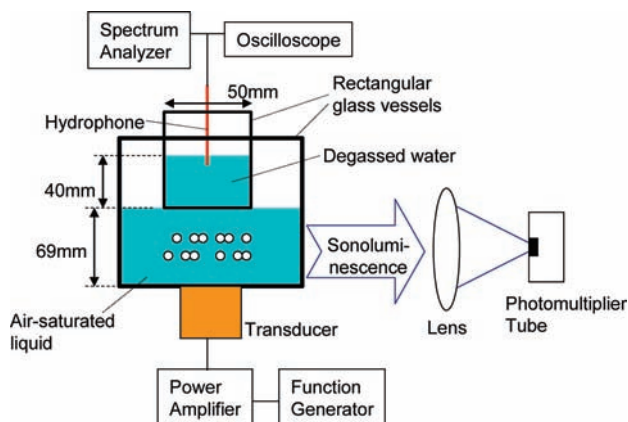* Corresponding author. E-mail: tuziuti.ni@aist.go.jp.

Figure 1. Experimental apparatus.

the wave, and as a result, the wave may gradually acquire a sawtooth shape.

2. Experimental Details

Figure 1 shows the experimental setup used in this study. A continuous sinusoidal signal at 141 kHz from a function generator (NF, 1942) was amplified by a power amplifier (ENI, 2100 L) to drive a Langevin-type transducer with a diameter of 45 mm. The transducer was attached to a circular stainless steel plate with a diameter of 100 mm (1 mm in thickness) set at the bottom of a rectangular glass vessel (in the figure, the larger vessel with inner dimensions of $170 \times 170 \times 150$ mm). A small glass vessel, with inner dimensions of $50 \times 50 \times 140$ mm and a bottom thickness of 1 mm, was positioned above the larger vessel. The air-saturated liquids used in this study were pure water, aqueous solutions of 1 mM SDS (Wako), 10 mM SDS, 1 mM SDS plus 0.1 M NaCl (Wako), 1 mM polysorbate20 (Tokyo Chemical Industries), and 10 mM polysorbate20, which were poured into the larger vessel to a liquid height of 69 mm. The smaller vessel was filled with degassed water to a liquid height of 40 mm. The liquid temperature was 25 °C.

If the pressure waveform is measured using a hydrophone that is directly immersed in the bubble-containing liquid, it is difficult to avoid the possibility of attachment of bubbles to the hydrophone. This has a significant effect on the measurements since the pressure variations due to bubbles close to the hydrophone can be intense compared with those in the surrounding regions. Indeed, Neppiras showed that subharmonic noise was reduced after cavitation bubbles attached to the hydrophone were removed.[13] Therefore, in this study, the hydrophone (RESON, TC4038) was set at the antinode nearest to the surface of a volume of degassed water in the upper small vessel far from the bubble layer. The pressure waveform was measured with a digital oscilloscope (YOKOGAWA, DL1540C). Frequency spectra of the pressure waveform were recorded by a spectrum analyzer (SONY Tektronix, 3026) at different applied transducer power levels, and the magnitudes of the fundamental ($f = 141$ kHz) and higher harmonics ($2f$, $3f$, $4f$, and $5f$) above the background level were measured.

The intensity of the sonoluminescence from the air-saturated liquids in the large vessel was measured with a photomultiplier tube (PMT) (Hamamatsu, R928). Data were recorded by a microcomputer (NEC, PC-9821 Xc16) through a digital multimeter (ADVANTEST, TR6847) which read the output voltage from the PMT.

It was assumed that the upper solution remained degassed for the duration of the experiment, since no SL could be detected

when the upper vessel was later set against the transducer plate and sonicated.

3. Results and Discussion

3.1. Pressure Waveform. Figure 2 shows the dependence of the measured pressure waveform on the power applied to the transducer. Note that each curve is normalized by its maximum amplitude. In Figure 2a (water), it can be observed that the waveform becomes distorted at high power levels. The curve has a steeper gradient for positive pressures and a broadened minimum for negative pressures. This is similar to the numerical results reported by Vanhille and Campos-Pozuelo at 200 kHz.[9] In Figure 2b (1 mM SDS), very little distortion is seen in the waveform, even at high power. In Figure 2c (10 mM SDS), the waveform is moderately distorted at intermediate power levels but only slightly at higher power. These effects may be related to a change in the spatial distribution[10] of bubbles with applied power.

According to the experimental results of Negishi[14,15] and the calculations of Colonius et al.,[16] Karpov et al.,[17] and Vanhille and Campos-Pozuelo,[18] formation of a sawtooth waveform occurs at relatively low frequencies (around 20 kHz) and high acoustic amplitudes. At low frequencies, bubbles are easily enlarged in the rarefaction phase and collapse violently leading to the emission of strong shock waves, and this increased contribution from the bubbles gives rise to the sawtooth waveform. However, in the present experiment, the frequency (141 kHz) was sufficiently high for this effect not to occur.

Several theoretical studies have been carried out on the sound field distribution during sonochemistry. Servant et al.[19] reported numerical calculations for an acoustic field in a sonochemical reactor using fluid dynamics simulations and taking into account the effect of bubbles and fluid motion. Yasui et al.[20] calculated the spatial distribution of the acoustic amplitude in a sonochemical reactor using the finite element method (FEM) considering the attenuation of ultrasound caused by bubbles. It is hoped that the findings of this study on waveform distortion by bubbles will prove useful for improving such calculations.

3.2. Frequency Spectra. Figure 3 shows the measured frequency spectrum as a function of applied power to the transducer. It is apparent that only integer harmonic components are present.

Plotted in Figure 4 is the applied power dependence of the intensity of the spectral components (f to $5f$) corrected for the background level measured in the absence of sonication. It can be seen that, for both water and 10 mM SDS, high harmonics began to appear at around $1-2$ W, whereas for 1 mM SDS such harmonics did not appear until much higher power levels (around 8 W). It is noticeable that for water, 1 mM SDS, and 10 mM SDS the intensity of the $5f$ component is relatively large at high applied powers, while that of the $2f$ component is small. The mechanism for this may be related to the aggregation of bubbles.[21] This tendency is different from that for the development of ultrasound waveform distortion due to the nonlinearity of a medium.[12] The ultrasound energy transfers in turn from the fundamental to higher harmonics ($2f$, $3f$, $4f$,...), resulting in a decreasing intensity for higher order components.

3.3. Sonoluminescence. In this section, a comparison is made between the cavitation threshold determined by the appearance of the high harmonics shown in Figures 3 and 4 and the threshold for sonoluminescence. Figure 5 shows the measured dependence of sonoluminescence intensities on the applied power to the transducer. The thresholds for SL in water, 1 mM SDS, and 10 mM SDS were 3.5, 8.3, and 9.4 W, respectively.
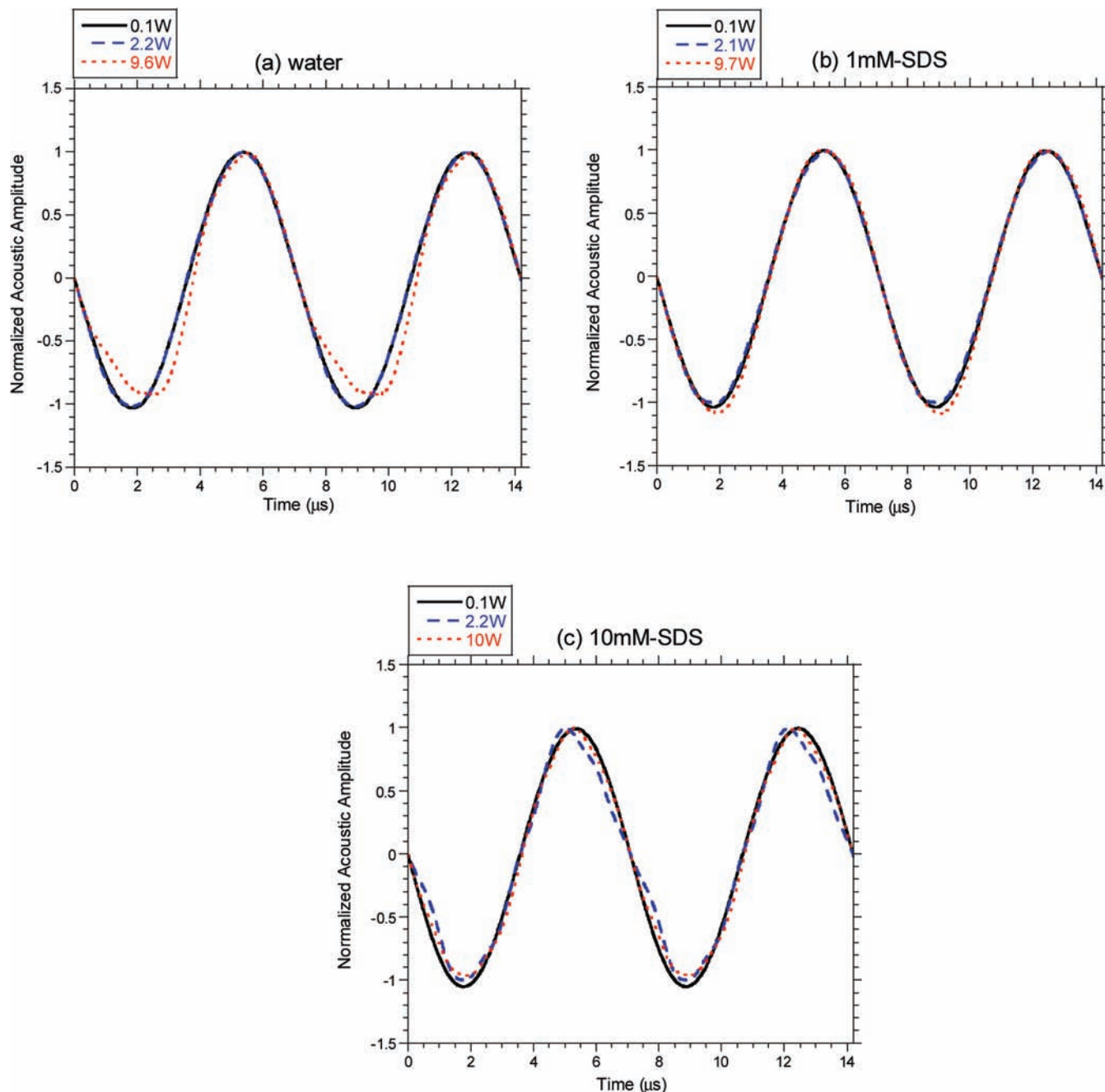
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Figure 2. Measured pressure waveforms for different applied powers to the transducer.

In each case, the threshold for SL is close to that for cavitation noise, as shown in Figure 4. The case for 10 mM SDS is different in that there is an intermediate region of acoustic amplitude between the SL and noise thresholds, and in this region there are bubbles that act as sound sources but do not collapse. This is consistent with the findings of Young[22] that there is emission from stable cavitation bubbles at acoustic intensities below the transient threshold.

Lee et al. performed a comparison between the SL activity of water, 1 mM SDS, and 10 mM SDS using the difference in dissolution of SL-emitting bubbles in the off cycles during pulsed operation.[10] In that investigation, it was deduced that the bubble size is smallest in 1 mM SDS and largest in water. Even if bubbles can exist in 1 mM SDS in the intermediate range of acoustic amplitude, the bubble size may be too small to generate cavitation noise or SL. According to Ashokkumar et al.,[23-25] considerable electrostatic repulsion occurs between

bubbles in 1 mM SDS since SDS is an anionic surfactant and it causes the surfaces of bubbles to become negatively charged. This effect inhibits bubble coalescence and keeps the bubble size small. It is known that when micrometer-sized bubbles exist, viscous resistance is effective at the bubble surface[26] and adsorption and desorption of surfactants at the surface can lead to acoustic energy loss by radial motion of the bubble.[27] This leads to a decrease in the acoustic amplitude and suppresses the development of nonlinearity in the waveform, which explains why little distortion of the waveform appeared in the case of 1 mM SDS. Figure 6 shows the total power detected by the hydrophone, summed over the f to $5f$ harmonics, as a function of applied power to the transducer. As can be seen, the acoustic intensities for water and 10 mM SDS are higher than that for 1 mM SDS except at the highest power. Accordingly, at 1 mM SDS, the nonlinearity can be weaker than that in water and 10
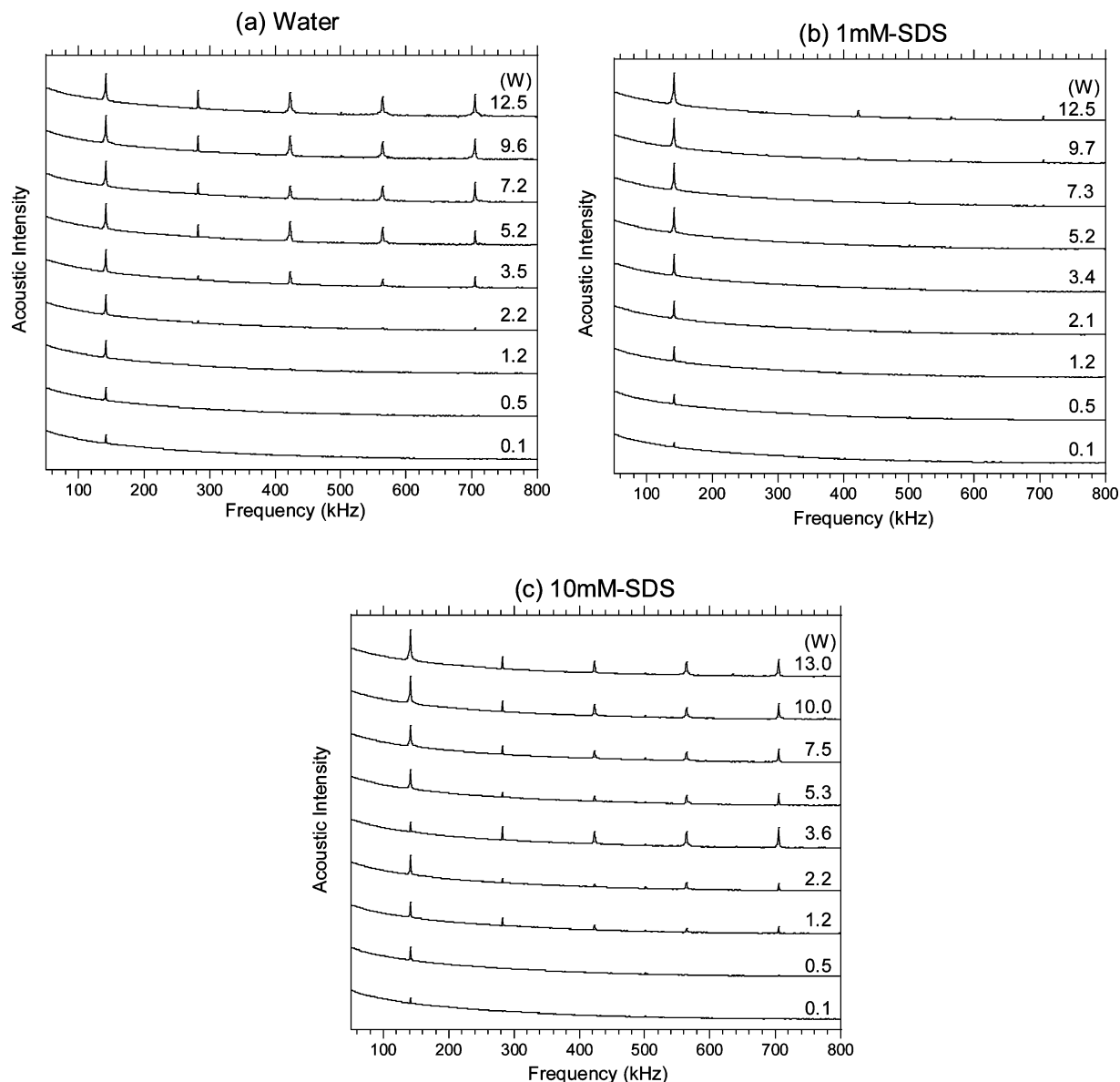
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Figure 3. FFT spectra for different applied powers to the transducer.

mM SDS. This is consistent with the smaller amount of waveform distortion in 1 mM SDS compared to water and 10 mM SDS.

Ashokkumar et al.[25] explained the frequency spectra of SDS aqueous solutions under sonication in terms of the prevention of bubble coalescence and declustering of bubbles within a cavitating bubble cloud. As mentioned above, a smaller amount of broadband noise occurs for low SDS concentration solutions (less than 3 mM) compared with the case for water or high SDS concentration solutions (more than 3 mM). As shown in this study, in order to form a better understanding of the ultrasonic cavitation field, it is important to observe not only the frequency spectrum but also the pressure waveform. Note that, in this paper, differences in the spectra and waveforms as a function of acoustic amplitude have been first identified between water and SDS solutions.

3.4. Influence of Addition of Electrolyte. In this section, the behavior of a 1 mM SDS solution in the presence of 0.1 M NaCl as an electrolyte is reported. The existence of the electrolyte is assumed to cancel the charge effect caused by low concentrations of SDS. Figure 7 shows the applied power dependences of the (a) waveform, (b) FFT spectra, and (c)

spectral components from f to $5f$. It is found from Figure 7a that the waveform is subject to distortion at high power (9.7 W), and the trend is similar for SDS and water. This is consistent with literature reports of higher cavitation noise in 1 mM SDS solutions in the presence of electrolytes.[24] The results for SL in 1 mM SDS + 0.1 M NaCl shown in Figure 5 and the spectral components seen in Figure 7c indicate that there is an intermediate region of applied power from the threshold for noise (1.5 W) to that for SL (8.5 W), which is similar to at the case for 10 mM SDS described above. It is seen in Figure 6 that the detected power for 1 mM SDS + 0.1 M NaCl is almost the same as that for 1 mM SDS except at the highest power setting. It is possible that the addition of electrolyte causes a weak clustering of bubbles while keeping the bubble size unchanged.

3.5. Influence of Nonionic Surfactant. In this section, the results for the solutions with 1 mM and 10 mM polysorbate20 added as a nonionic surfactant are reported. In this case, no charge effect similar to that for SDS at low concentration is expected and there is a possibility of coalescence or clustering of bubbles. Shown in Figures 8 and 9 are the applied power dependences of the (a) waveforms, (b) FFT spectra, and (c)
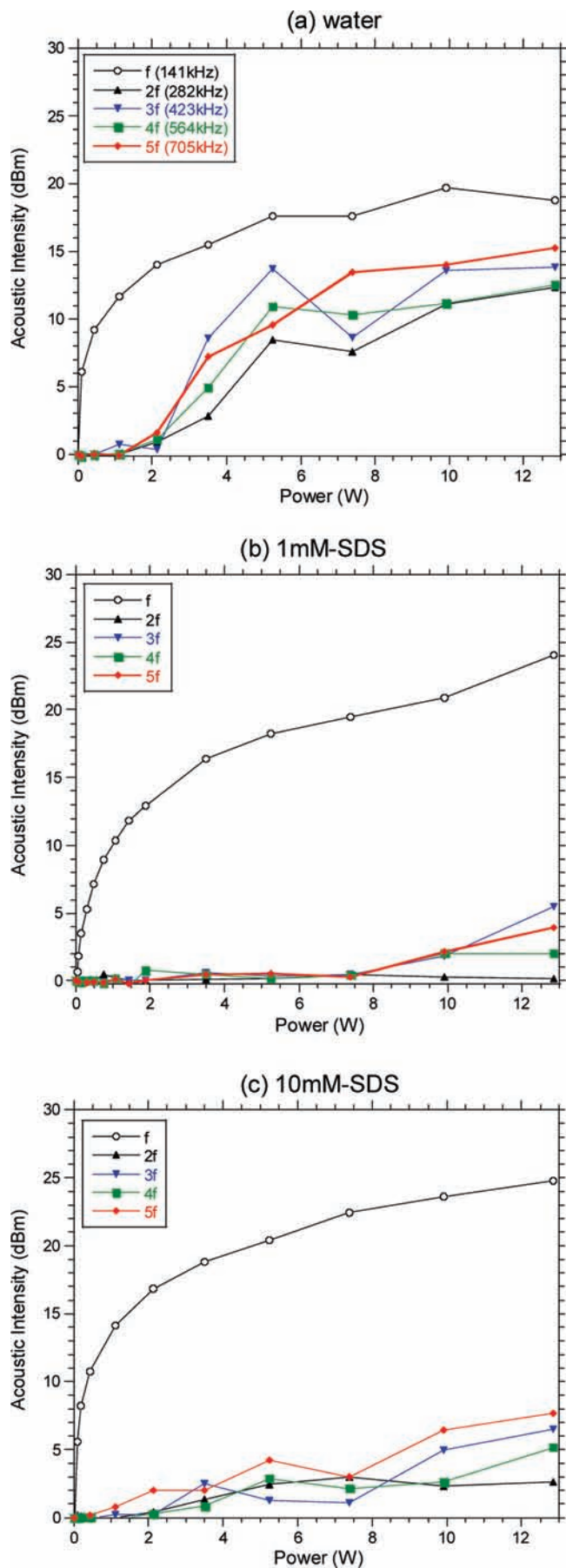
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Figure 4. FFT-spectral components from fundamental (*f*) to higher harmonics (2*f*, 3*f*, 4*f*, and 5*f*) as a function of applied power to the transducer.
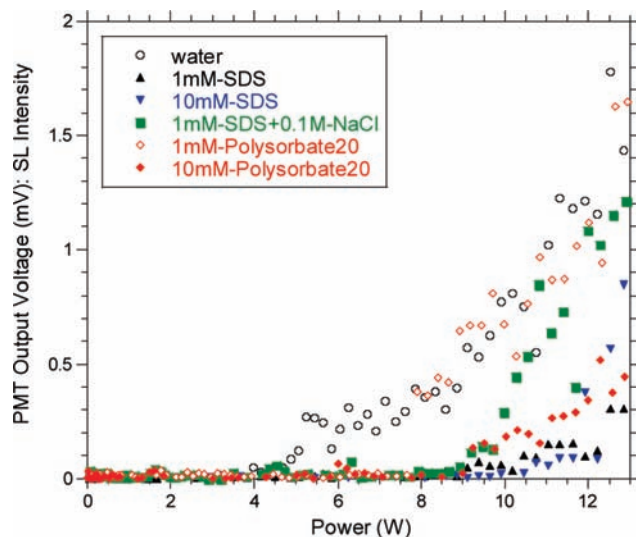

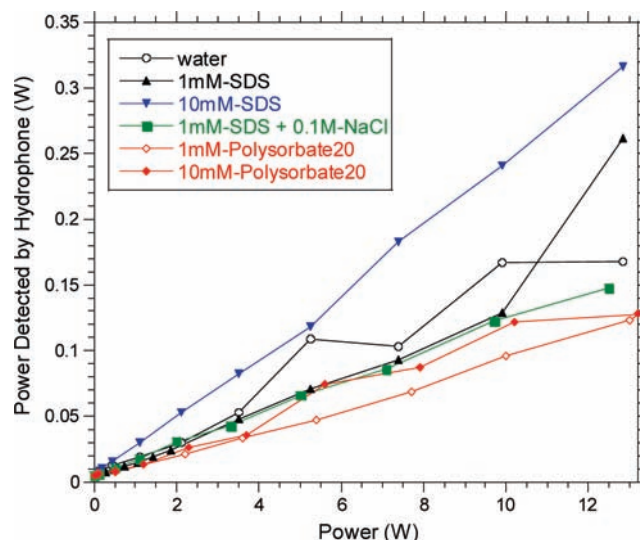**Figure 5.** SL intensities as a function of applied power to the transducer.

Figure 6. Integrated detected power from *f* to 5*f* as a function of applied power to the transducer.

spectral components from *f* to 5*f* for 1 and 10 mM solutions, respectively.

The SL results for 10 mM polysorbate20 seen in Figure 5 and the spectral components in Figure 9c suggest that there is an intermediate region of applied power from the threshold for noise (around 1 W) to that for SL (9 W), which is similar to the case for 10 mM SDS. This intermediate region would correspond to the existence of large-sized stable bubbles. This is not found to be the case for 1 mM polysorbate20, where the thresholds were almost the same (8 W) (Figures 5 and 8c).

Comparing the spectral components of 1 mM SDS (Figure 4b) and 1 mM polysorbate20 (Figure 8c) in the high power region (from around 8 W to the highest power setting), it is found that the ratio of the higher harmonics to the fundamental component for polysorbate20 is higher than that for SDS. This means that in the nonionic solution there is some coalescence between bubbles causing the bubble size to become large enough to overcome the viscous resistance inhibiting the pulsating motion.

Comparing Figures 8a and 9a at high power, it is seen that the waveform distortion for the 10 mM solution was more than that for the 1 mM solution. It is also found from Figures 8c
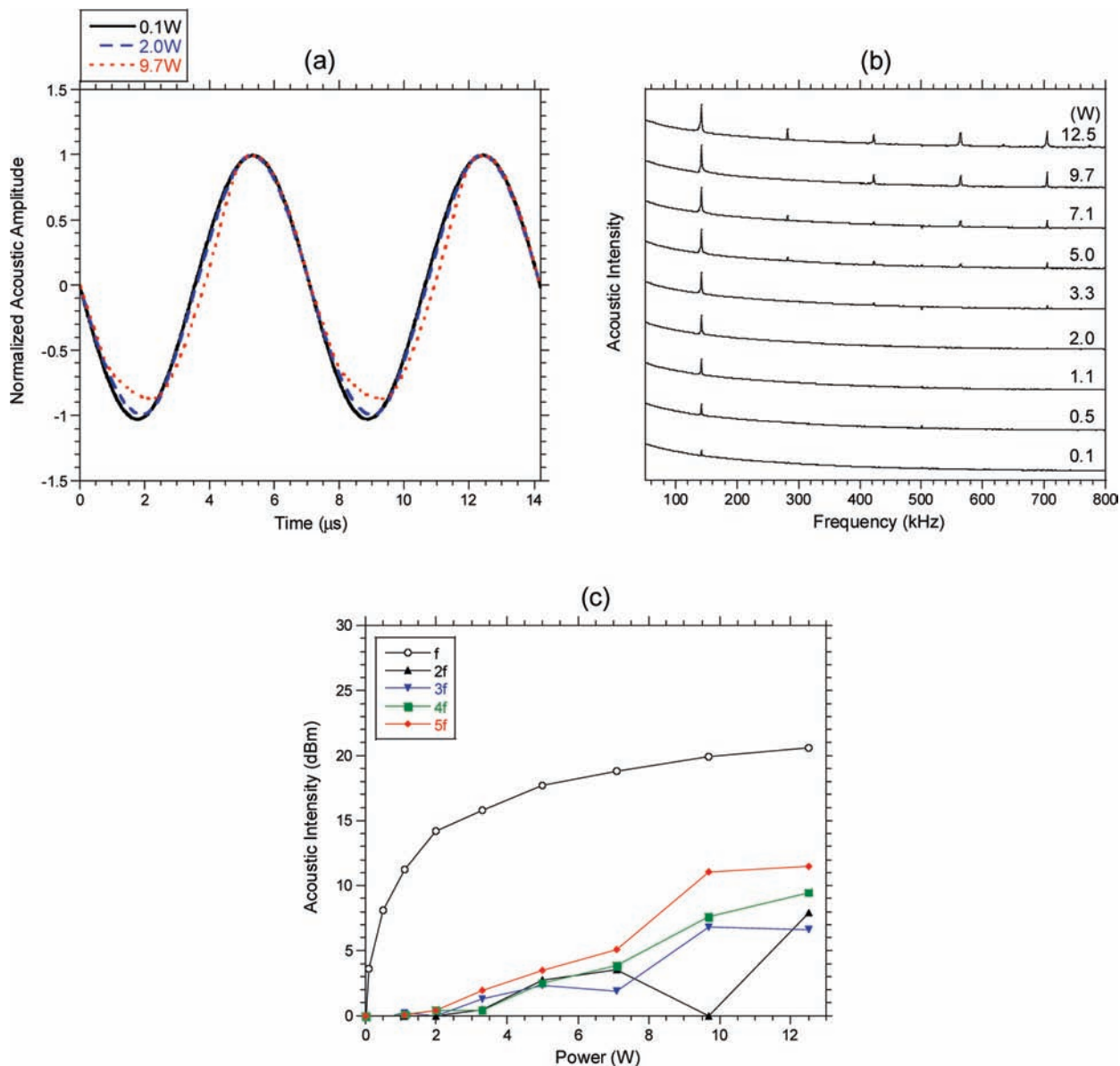
Figure 7. Measured pressure waveforms, FFT spectra, and integrated FFT-spectral components for various applied powers for 1 mM SDS + 0.1 M NaCl.

and 9c that the nonlinear trend is more remarkable for the 10 mM solution. Although the initial bubble size in the 10 mM solution may be smaller than in the 1 mM solution, the size of clusters created by the aggregation of daughter bubbles ejected from a mother bubble[28] can be larger in the former case. There is a possibility that such clusters coalesce to give rise to larger bubbles by means of the secondary Bjerknes force. As the bubble size becomes larger, the loss of acoustic energy due to adsorption and desorption of surfactant molecules is reduced and the acoustic amplitude can become higher. Indeed, the detected power for 1 mM polysorbate20 was lower than that for 10 mM polysorbate20, as shown in Figure 6.

Larmignat et al.[29] measured the size of bubbles in solutions containing various concentrations of polysorbate20, where the bubbles were produced by stirring the solution in a baffled beaker under no sonication. Their results indicated that there are small differences in bubble size which may be attributed to a slight change in the surface tension in the range from 0.21 to 77.77 mM. Further study on the influence of sonication on the bubble size in solutions containing polysorbate20 is required.

4. Conclusions

The small amount of distortion of the waveform for low SDS concentration (1 mM) may be attributed to a lower population of large coalesced bubbles due to electrostatic repulsion, which leads to damping of the sound energy and little cavitation noise because of viscous resistance to bubble radial motion in addition to adsorption and desorption of surfactant molecules at the bubble−liquid interface. The distorted waveform in water was found to have a curve with a steeper gradient for positive pressures and a broadened minimum for negative pressures, which is in reasonable agreement with the theoretical waveform. The addition of an electrolyte (0.1 M NaCl) or nonionic surfactant (10 mM polysorbate20) led to additional distortions to the waveform. At high SDS concentration (10 mM), the waveform was also distorted, possibly because the excess SDS molecules were playing the role of an electrolyte. Electrolytes which can cancel the charge of bubbles and reduce the electrostatic repulsion between them will permit clustering of bubbles and the creation of large-sized bubbles by coalescence. The size of bubbles at 10 mM SDS can be larger than that at 1
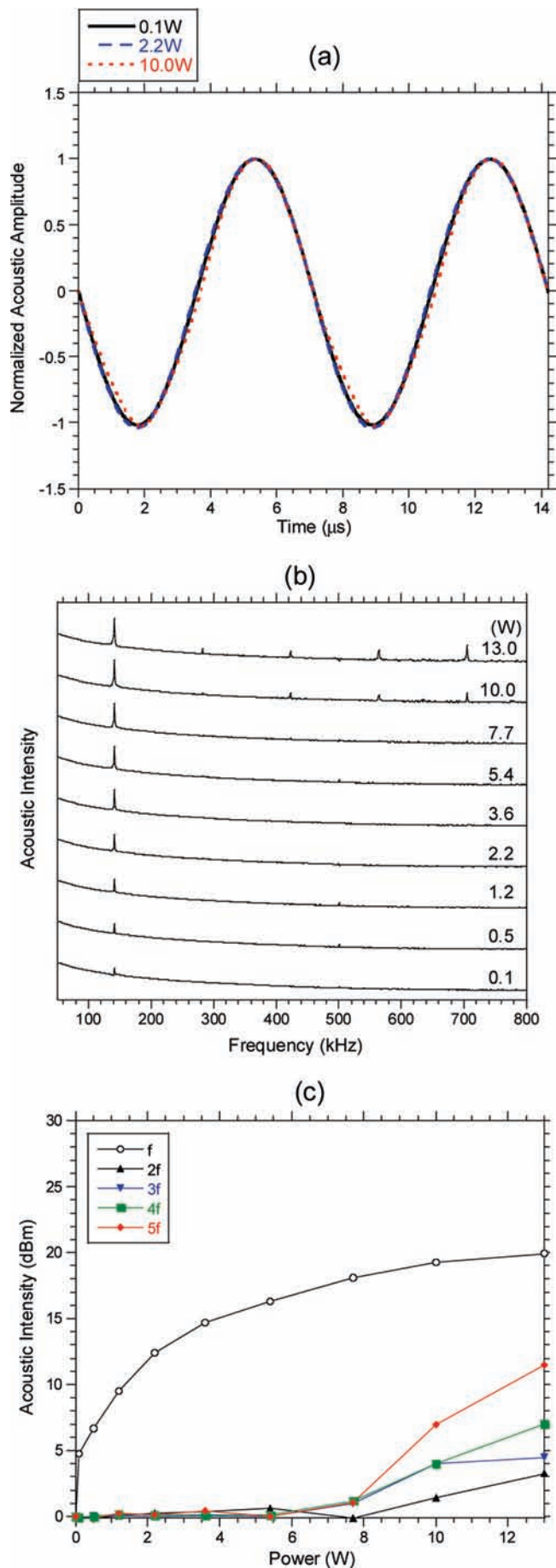
Figure 8. Measured pressure waveforms, FFT spectra, and integrated FFT-spectral components for various applied powers for 1 mM polysorbate20.
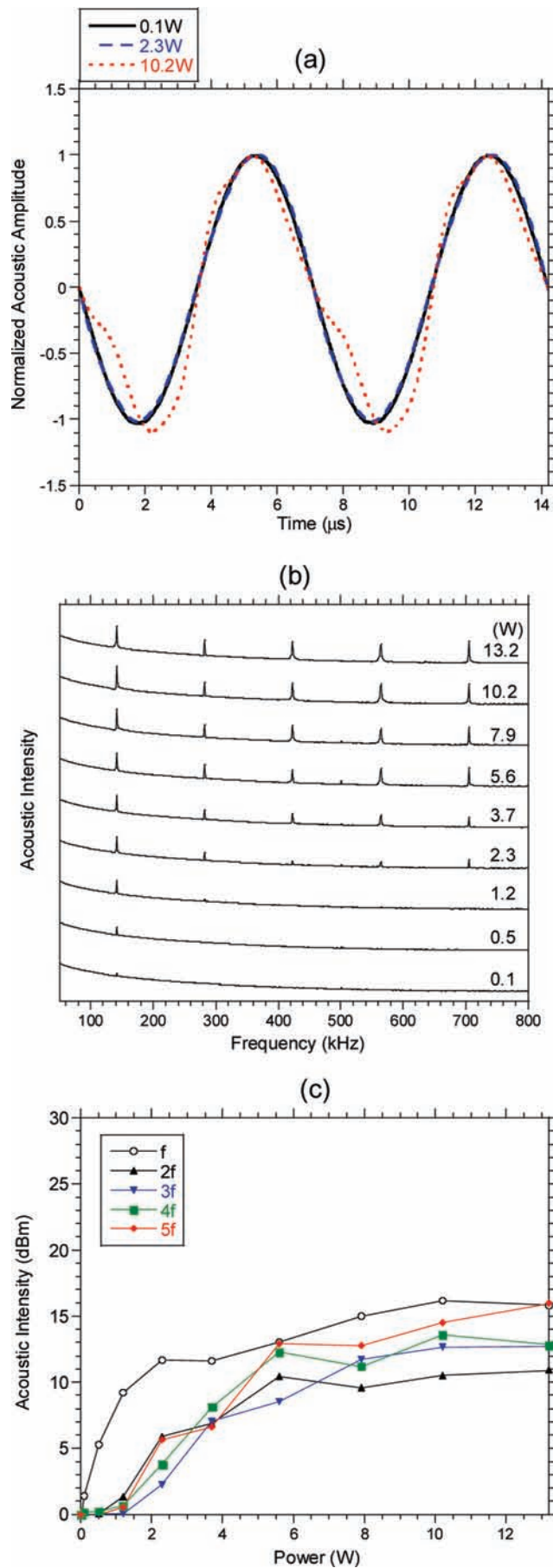
Figure 9. Measured pressure waveforms, FFT spectra and integrated FFT-spectral components for various applied powers for 10 mM polysorbate20.

mM, and the energy damping at 10 mM is relatively low leading to the waveform distortion. The intermediate region of applied power between the threshold for cavitation noise and that for SL would imply the existence of large-sized stable bubbles.

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