Destabilization of ultrafine bubbles in water using indirect ultrasonic irradiation

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ABSTRACT

Ultrafine bubble (UFB) is a bubble with a diameter of less than 1 μm. Little attention has been paid to the defoaming and removal of UFBs. This study proposes a method to destabilize UFBs by using indirect ultrasonic irradiation. Besides, the destabilization mechanism of UFB was investigated. The ultrasonic frequency was 1.6 MHz and the dissipated power was 30 W. UFB dispersions were prepared using two different types of bubble generators: pressurized dissolution method and swirling liquid flow method. The effects of ultrasonic irradiation on the stability of UFBs were evaluated by particle tracking analysis (PTA) and electrophoretic zeta potential measurement. Results showed that the indirect ultrasonic irradiation for 30 min reduced the number concentration of UFBs by 90% regardless of the generation method. This destabilization was attributed to a decrease in the magnitude of zeta potential of UFBs due to the changes in pH and electrical conductivity. These changes in the electrochemical properties were caused by the formation of nitric acid. To study the destabilization mechanism, the pH of the UFB dispersions were modified by titration; the chemical and mechanical effects of ultrasound were separately examined. It was found that not only the chemical effect caused by the formation of nitric acid but also the mechanical effect contributed to the destabilization of UFB. Feasibility studies were also performed for UFBs in an aqueous surfactant solution and UFBs in a solid particle dispersion. The proposed method selectively destabilized UFBs in the solutions.

1. Introduction

Ultrafine bubble (UFB) is a bubble, which has a volume equivalent diameter of less than 1 μm. It has also been called “nanobubble” or “bulk nanobubble.” In 2017, the International Organization for Standardization (ISO) published a standard that defines the technical terms of fine bubble technology [1]. In the standard, the ISO refers to the use of the term “ultrafine bubble” instead of “nanobubble.” Therefore, in this paper, we only use “ultrafine bubble” rather than “nanobubble” or “bulk nanobubble” although they refer to the same subject.

Before the international standard was published, researchers have been studied the potential applications of UFBs in various fields, such as cleaning [2,3], flotation [4,5], water treatment [6,7], medicine [8,9], and aquaculture [10,11]. Even though the stabilization mechanism for UFB remains controversial, many researchers have found that UFBs do exist, based on the numerous experimental evidence. Recently, Azevedo et al. [12] have reported a careful review of the basic properties of UFBs. After reviewing more than 150 papers, they concluded that UFBs can remain stable for weeks and months. To accelerate a sound discussion, research on the fundamental properties of UFB should be advanced.

Generation and destabilization of UFBs are of fundamental and practical importance in many applications. Concerning the generation of UFBs, several researchers have reported various methods such as pressurized dissolution [13,14], swirling liquid flow [10,15], ultrasonic irradiation [16,17], and membrane method [18]. On the other hand, only a few have studied the defoaming and removal of UFBs from liquid media. Nirmalkar et al. [16] studied the effect of the freeze–thawing process on the stability of UFBs that were acoustically generated in pure water and the solution of sodium dodecyl sulfate (SDS). They reported that the cycles of freeze–thawing effectively destabilize UFBs in pure water, but not in the surfactant solution. Another method is reported by Yasuda et al. [17]. They exposed pure water to ultrasound at various...
frequencies (22–1000 kHz) of 15 W and determined the rate constants for UFB generation and reduction. They concluded that the rate of UFB generation is higher at lower frequencies, whereas that of UFB reduction is higher at higher frequencies. To the best of our knowledge, these two methods are known to effectively destabilize UFBs. However, the freeze–thawing method is unsuitable to destabilize UFBs in a surfactant solution, and direct ultrasound irradiation has the potential for contamination of the liquid by erosion.

Here, we propose a method to destabilize UFBs by using indirect ultrasonic irradiation, which is less contaminating. The destabilization mechanism of UFBs is discussed in relation to the zeta potential of UFBs and liquid properties such as electrical conductivity and pH. We also demonstrate a feasibility study of the ultrasonic irradiation on the stability of UFBs in an aqueous surfactant solution and in the mixture with polystyrene latex beads having a nominal diameter of 300 nm.

2. Materials and methods

2.1. Materials

Purified water having an electrical conductivity of 5.5 μS m−1 was prepared by a water purifier (Milli-Q, Merck). This water is referred to as pure water throughout this paper. Sodium hydroxide (NaOH, 97%, Kanto Chemical Co., Japan) and nitric acid (HNO₃, 60%, Kishida Chemical Co., Ltd., Japan) for pH adjustment were used for pH adjustment without further purification. A nonionic surfactant, polyethylene glycol monocetyl ether was also purchased from Tokyo Chemical Industry Co., Ltd. This surfactant has the chemical formula of (C₂H₄O)nC₁₆H₃4O with a molecular weight of approximately 1100 g mol⁻¹ and has been used in food, cosmetic, and pharmaceutical applications. The number concentration of foreign particles such as dust particles in the aqueous solution of these chemicals was measured before each experiment using the particle tracking analysis instrument (described later) and confirmed to be below the lower detection limit (< ~1 × 10⁷ particles mL⁻¹).

2.2. Ultrafine bubble generation and storage

UFB dispersions were prepared using two different commercial UFB generators. One is a swirling liquid flow type, Microstar (FS300DC-SW1, Fuki Co., Ltd, Japan), which generates bubbles by strong shear force [19,20], and the other is a pressurized dissolution type [21,22]. Ultrafine GaLF (FZ1N-10, IDEC Co., Japan), the gas induced into the generator was ambient air filtered through a polypropylene hollow fiber membrane having a pore size of 10 nm (KIC-T6, KITZ MICRO FILTER Co., Japan). The UFBs and their dispersions produced by Microstar are referred to as UFB-M, and those produced by Ultrafine GaLF are referred to as UFB-G. Prepared UFB dispersions were stored in disposable 30-mL glass vials for further analysis. The concentration of total organic carbon (TOC) of both UFB dispersions was determined to be less than 0.4 mg L⁻¹, which was measured by a TOC analyzer (TOC-VCSH, Shimadzu Co., Japan).

Comparing the two generation methods, the pressurized dissolution method seems to be more advanced for industrial use. For instance, dissolved air flow (DAF), commonly known as one of the flotation processes, uses a bubble generation mechanism similar to the present method. A typical bubble generator of this method consists of a pressurized dissolution tank, centrifugal pump, and reservoir vessel. Many generators have built-in aspirators. The aspirated gas is mixed with the liquid in the pressurized tank and this process creates a dissolved gas supersaturation. When the supersaturated liquid flows into the reservoir vessel, which is under atmospheric pressure, bubbles including UFBs are thought to be generated [23]. In many cases, the supersaturation, i.e., the supersaturation pressure in the pressurized dissolution tank, is optimized by the manufacturers. The supersaturation pressure of typical commercial generators is set to be around 200–500 kPa gauge. IDEC’s Ultrafine GaLF uses a gauge pressure of 300 ± 20 kPa as the optimized value for UFB generation. The effect of supersaturation pressure on UFB generation is summarized in the review by Azevedo et al [12].

Another method is the swirling liquid flow method used to generate UFB-M. This method has been less studied than the pressurized dissolution method. However, as mentioned in the Introduction, interesting applied research has been reported using the UFBs generated by this method [10,24]. Although most of the generators of this method aspirate gas, the introduced gas is not dissolved in the liquid under pressure, but is torn apart by strong shear force and dispersed as microbubbles. UFBs are thought to be produced with the generation of microbubbles [23]. Although the two different UFB generation systems have been outlined above, little research has elucidated the principle of UFB generation, and no widely accepted theory has been developed.

2.3. Experimental setup

Fig. 1 shows a schematic of the experimental setup. Indirect ultrasonic irradiation was performed with an ultrasonic cleaner (QUAVA mini, Kaijo Co., Japan). The ultrasonic frequency was 1.6 MHz and the displayed load power was set to be 100 W. The reactor was a 30-mL glass vial with a screw lid and the sample volume was 15 mL. Pure water in the acrylic vessel was almost air-saturated.

The distance between the reactor and the transducer was fixed at 40 mm to keep the irradiation conditions constant. According to the manufacturer, the distance should be at least 30 mm to ensure proper ultrasound exposure and to avoid damaging the transducer. Although there is still room to increase the ultrasonic efficiency by optimizing the reactor-to-transducer distance and deaeration of the ultrasonic transmission medium, the distance fixed at 40 mm made the experiments very reproducible, as will be discussed in the Results and discussion.

The output power determined by the calorimetric method [25] using a thermocouple (K-type, T35, Sakaguchi E.H VOC Co., Japan) and data logger (NR-TH08, Keyence Co., Japan) was 30 W. Since the displayed load power was 100 W, the ultrasonic transmission efficiency was calculated to be 30%. This efficiency is considered to be reasonable for indirect irradiation [26].

2.4. DO, pH, and EC measurement

Dissolved oxygen concentration (DO) was measured using a fluorescence type oxygen meter (Seven2Go Pro, Mettler Toledo, US). Both pH and electrical conductivity (EC) were measured using a pH and EC meter (LAQUAact D-74, Horiba Ltd., Japan) at least three times at a sample temperature of 25 ± 1 °C.

2.5. Zeta potential measurement

Zeta potential measurements were performed using a zeta potential analyzer (ELSZ-2000Z, Otsuka Electronics Co. Ltd., Japan), which adopts the Doppler electrophoresis as the basic principle. Measurements
were repeated 3 to 5 times for each sample.

2.6. Particle size and concentration measurement

Particle size and number concentration of UFBs were evaluated using a particle tracking analysis (PTA) instrument (NanoSight NS300, Malvern Instruments, UK) with a violet laser light source (wavelength: \(\lambda = 405\) nm). The software for image analysis was NTA3.0 (Malvern Instruments, UK). The observation cell of the instrument has a temperature control that maintains the liquid temperature to \(25.0 \pm 0.5\) °C. Each measurement consisted of five movies of each 60 s long.

A description of PTA can be found elsewhere [27,28]. Briefly, PTA instruments estimate the hydrodynamic size of individual particles based on the Stokes–Einstein equation as shown in Eq. (1).

\[
d = \frac{k_B T}{3\pi \mu D_t}
\]

where \(d\) is the particle diameter, \(k_B\) is the Boltzmann constant, \(T\) is the absolute temperature, \(\mu\) is the dynamic viscosity and \(D_t\) is the translational diffusion coefficient. PTA instruments analyze the particles under Brownian translational motion and calculate the diffusion coefficients using the following equation:

\[
D_t = \frac{(x,y)^2}{4t}
\]

where \((x,y)^2\) is the mean squared displacement of a particle in two dimensions and \(t\) is the time between sequential displacement measurements, i.e., the frame to frame period [28].

In most PTA systems, the two-dimensional motion of the center of scattered light corresponding to each particle is captured as a movie, and the movie is analyzed by an image analysis software. The system for image acquisition and image analysis differs from manufacturer to manufacturer. In the case of the NanoSight system, there are two important measurement parameters: camera level and detection threshold. Camera level is a parameter for image acquisition that controls the gain and shutter speed, whereas the detection threshold is a parameter for image analysis that determines the minimum brightness of pixels considered to be single particles. These two parameters have a large influence on the particle concentration and size measurement and should be optimized before the measurements depending on the refractive index of both particles and solvent [29]. In this study, therefore, we carefully adjusted the camera level in the range of 9–15 and the detection threshold in the range of 5–12, depending on the scattering intensity of the samples.

PTA instruments indicate the number of particles in the field of view and can estimate the number concentration of particles under observation. In the PTA system used in this study (NanoSight NS300 and NTA3.0), the number concentration is proportional to the number of particles tracked within the field of view. The proportionality coefficient is approximately \(2.0 \times 10^7\) particles mL\(^{-1}\). Thus, for instance, if ten centers of scattered light are observed, the number concentration is...
calculated to be $2.0 \times 10^8$ particles mL$^{-1}$.

The NanoSight system collects not only particle size and number concentration but also the scattering intensity of each individual particle. In the Rayleigh scattering regime, where the ratio of the particle diameter to the wavelength of the incident laser is approximately less than 0.1, the scattering cross-section, which is the efficiency of light scattering, $\sigma_s$, is given by Eq. (3) [30].

$$\sigma_s = \frac{2\pi^3}{3} \frac{d^6}{\lambda^2} \left( \frac{n_1^2 - 1}{n_2^2} \right)^2$$  \hspace{1cm} (3)

where $\lambda$ is the wavelength of the incident laser, and $n$ is the ratio of the particle refractive index to the solvent refractive index. According to this equation, the scattering intensity is proportional to the sixth power of $d$ and a function of $n$. It is clear from Eq. (3) that different refractive indices give different scattering intensities, even if the particles have the same size. Fig. 2 shows a PTA result of the size standard of 100-nm polystyrene latex (PSL) beads (3100A, Thermo Fisher Scientific, US). According to the vendor, the CV (coefficient of variation) of the particle size distribution of the PSL beads, determined by electron microscopy, is 6.8%. Because the PSL beads have such a narrow size distribution, a single peak can be found in the size distribution (Fig. 2a). Results for light scattering intensity also reflect this uniform size distribution: one of the captured images of scattered light centers (Fig. 2b) and three-dimensional (3D) histograms of intensity vs. diameter vs. counts (Fig. 2c,d).

The 3D histogram is not created automatically from the NTA software (NTA3.0) but can be created using a graphics software. In this study, 3D histograms were created using a CSV (comma-separated values) format data called “Particle Data”, which were output from the PTA software. Data called “Ln (Adjusted intensity)” and “Size” in the CSV were recomposed using MATLAB (MathWorks, Inc., US) and its “hist3” function. These 3D histograms show a plot of mean scattered light intensity (natural logarithm of modified intensity) vs. diameter vs. the absolute number of counted particles. They quantitatively illustrate the scattered light intensity of the particles and particle size. For instance, when particles having the same size but different refractive indices are present, two peaks having different scattering intensities can be detected [31]. That is, we can qualitatively compare the relative scattering intensity, or refractive index, from the position of the peaks on the 3D histogram.

3. Results and discussion

3.1. Effect of indirect ultrasonic irradiation on the stability of UFBs

First of all, we describe the flow of the sample and the behavior of visible bubbles in the liquid bulk during ultrasonic irradiation. A short video showing the fluid flow and bubble motion in a blank sample (pure water) during ultrasonic irradiation is available online, a link to which is shown in the Appendix. The indirect ultrasonic irradiation of 1.6 MHz agitated the surface and bulk of the sample. As evidenced by the video, visible bubble motion was observed in the liquid bulk. Although this video is an example of a blank sample (pure water), the same flow was observed in the UFB dispersions. Therefore, it can be said that the presence or absence of UFB does not change the liquid flow or observable bubble behavior.

Before discussing the effects of ultrasonic irradiation on the size, number concentration, and zeta potential of UFBs, the effect of liquid temperature on the stability of UFBs was quantified in a preliminary experiment because ultrasonic irradiation in the absence of refrigeration raises the liquid temperature of the sample. As a result of ultrasonic irradiation for 30 min, which is the maximum irradiation time in this study, the sample temperature increased from 23 °C to 37 ± 1 °C. In order to discuss only the effect of this temperature increase, the following experiments were performed: the UFB dispersions were placed in a warm bath at 40 °C for 1 h, and the size, number concentration, and zeta potential of UFBs were measured before and after the heating in the bath. This preliminary experiment revealed that the increase in water temperature does not affect the stability of UFB in the range from room temperature to 40 °C; the transient elevation of temperature did not change the size or number concentration or zeta potential of UFBs (data not shown). Therefore, the chemical and mechanical effects of ultrasonic irradiation other than the increase in the liquid temperature will be discussed. Ideally, the ultrasonic propagation medium should naturally be cooled. By doing so, a uniform sound field in the sample and the propagation medium is expected to be achieved. Therefore, temperature control is one of the points to be improved in the future.

Fig. 3 shows the effect of ultrasonic irradiation on the size distribution of UFBs. The comparison of the size distributions of the two different UFB dispersions illustrates that the different generation methods resulted in different sizes. Since all measurements were made within approximately one week of the UFB generation, the effect of aging, e.g., aggregation, on the properties of the UFBs should have been approximately equal in both samples.

Despite the difference in size distribution, both UFBs were effectively destabilized by ultrasonic irradiation. As shown in Fig. 3a, the number concentration of UFB-M decreased sharply and the mode diameter slightly changed from 73 nm to around 60 nm. This shift indicates that the larger UFBs may have been destabilized first. As a result of ultrasonic irradiation for 30 min, the number concentration decreased to less than the detection limit (less than one particle per frame) of the PTA device. On the other hand, in the case of UFB-G (Fig. 3b), the mode diameter was shifted from 127 nm to 73 nm, while the number concentration was...
almost maintained. After the shift, the number concentration of UFBs decreased sharply.

Fig. 4 summarizes the effect of ultrasonic irradiation on the number concentration of UFBs. The number concentration of UFB-M decreased at the first 5 min to below 10% of the initial concentration while the number concentration of UFB-G decreased gradually to below $1 \times 10^8$ mL$^{-1}$. Since each plot consists of the average of 3 independent irradiation experiments, a total of 24 experiments were performed (12 times each). The top and bottom ends of the bars show the maximum and minimum values, respectively. The good quality of these overlapping data suggests that the proposed method is highly reproducible.

The scattering intensity distribution shown in the 3D histograms illustrates further interesting experimental results. The time variation of the size and scattering intensity distribution of the UFBs is shown in Fig. 5. For UFB-M, as the ultrasonic irradiation time increased, both the peak of size and scattering intensity decreased (Fig. 5a,b). On the other hand, for UFB-G, the size and scattering intensity distribution changed drastically: particles with high scattering intensity disappeared (Fig. 5c, d). Note that it is difficult for PTA instruments to simultaneously detect particles with different scattering intensities; only the particles with strong light scattering intensities are mostly measured [32]. Therefore, the gradual decrease in apparent number concentration found in UFB-G (Fig. 4) may be due to the faster reduction of larger UFBs, allowing smaller UFBs to be detected (Fig. 5c,d).

Another intriguing result can be seen from a comparison of the UFB-M and UFB-G when they are roughly the same size; Fig. 5a,d show that the two distributions are almost identical. This fact implies that the UFBs have the same degree of scattering intensity, i.e., the same degree of refractive index, even if the UFB generation method is different.

### 3.2. Effect of ultrasonic irradiation on the electrochemical properties

To understand the destabilizing mechanism of UFBs, we measured the zeta potential of UFBs. Time variation of the electrochemical
properties such as pH and electrical conductivity (EC) was also evaluated because these electrochemical properties are known to alter the zeta potential and thus have a large influence on the colloidal stability of nano- and submicron particles [33–35].

Fig. 6 shows the effect of ultrasonic irradiation on the zeta potential of UFBs. The zeta potential changed from approximately −30 mV to 0 mV as the ultrasonic irradiation time increased. For both UFB dispersions, the zeta potential became below −10 mV after 5 min from the start of ultrasonic irradiation. Since colloidal particles with a zeta potential of less than −20 mV are considered unstable [35], the degree of reduction in the absolute value of the zeta potential can reasonably explain the loss of the colloidal stability of UFBs. Because of the change in zeta potential, the UFBs may have coalesced, floated, and/or burst. It should be noted that it was not possible to observe the coalescence of UFBs during ultrasonic irradiation because the size of UFBs is much smaller than the visible range.

Fig. 7 shows the effect of ultrasonic irradiation on the electrochemical properties of the UFB dispersions. Temporal changes in pH were identical for the three samples (UFB-M, UFB-G, and blank). As the irradiation time increased, the pH decreased from neutral to approximately 3 (Fig. 7a). The EC also showed roughly the same temporal variation in the three samples; the values agreed within ±15% up to 15 min of irradiation (Fig. 7b). However, at the irradiation time of 30 min, the values of EC were varied; the mean values of blank (pure water) and UFB-G differed by more than 10 mS m⁻¹. It is unclear why the final EC values did not match exactly. Although it is interesting to discuss the cause of this difference, the focus of this study is on the destabilization behavior of UFBs, not the change in the liquid properties. Therefore, no further investigation was conducted. These are the topics that will be explored in the future.

Although the final EC values were somewhat different, the majority of the overlapping plots clearly show that the liquid properties changed with ultrasonic irradiation time regardless of the type of UFB generation method. It has been reported that the zeta potential of UFBs approaches zero at pH 2–4 [36,37]. Our results (Figs. 6 and 7a) are consistent with those reported. Therefore, the acidification of the dispersion is considered to be the main cause of the large change in zeta potential. In addition to the decrease in pH, the increase in EC (Fig. 7b), is known to reduce the colloidal stability of particles [35]. Based on the experimental results, we conclude that ultrasonic irradiation acidifies the dispersion and alters the zeta potential, resulting in a destabilization of UFBs.

Next, we consider the causal relationship between ultrasound irradiation and the changes in the electrochemical properties. The effect of ultrasonic irradiation on liquid properties has been investigated both experimentally and theoretically [38–40]. These studies showed that the reduction in pH was caused by the generation of nitric acid and other nitrogen oxides. For instance, Koda et al. [38] conducted an experiment to understand the effect of indirect ultrasonic irradiation on the pH of water. The ultrasonic irradiation at 540 kHz was conducted under an atmosphere of various gases such as air, oxygen, nitrogen, and argon. As a result of the 30-min ultrasonic irradiation, the pH of water changed from 7 to 4.3 under the air atmosphere, whereas the pH changed by less than 1 under the atmosphere of the other gases. They concluded that the formation of nitric acid, HNO₃, and nitrous acid, HNO₂, is the main cause of the pH decrease. Supeno and Kruus [39] also confirmed the formation of nitrite and nitrate in water under ultrasonic irradiation at 900 kHz. Yasui et al. [40] conducted numerical simulations to investigate the effect of ultrasonic frequency (20–1000 kHz) and pressure amplitudes (up to 10 bars) on the bubble temperature and main oxidant created inside a bubble. They simulated nonequilibrium chemical reactions in a pulsating air bubble and indicated the production of HNO₂ and HNO₃. Therefore, even in our case, these nitrogen oxides are suspected to be the main reason for the changes in the electrochemical properties.

To confirm the generation of these acids, we measured the concentration of nitrogen oxides using a water test kit (Packtest, Kyoritsu Chemical-Check Lab., Co., Japan). The measurement principle of the test kit for nitrate ion, NO₃⁻, and nitrite ion, NO₂⁻, is N-(1-Naphthyl)ethylendiamine colorimetric method. The water quality test was carried out in the same experimental setup and conditions of the ultrasonic irradiation for UFB destabilization. Table 1 summarizes the results of the water test for a blank sample (pure water). The dissolved oxygen
concentration (DO) remained constant. The longer the irradiation time, the more NO$_3^-$ was produced. On the other hand, NO$_2^-$ was hardly produced; the concentration of NO$_2^-$ was almost the same as the detection limit of the water test. These experimental results confirmed that the formation of HNO$_3$ decreased pH and increased EC. Note that the liquid temperature shown in Table 1 was measured simultaneously with DO by the DO meter and therefore does not reflect the increase in liquid temperature caused by ultrasound irradiation.

In summary, we propose the destabilization mechanism of UFBs as follows: (i) indirect ultrasonic irradiation produces nitrogen oxides, mainly NO$_3^-$; (ii) the formation of NO$_3^-$ lowers pH and increases EC; (iii) the changes in the electrochemical properties bring the absolute zeta potential close to zero and destabilizes UFBs.

### 3.3. Effect of pH on the stability of UFBs

Since the change in the electrochemical properties is a result of the chemical effects of ultrasound, another effect of ultrasound, namely the mechanical effect, needs to be considered. To study these effects separately, we altered the pH of UFB dispersions by adding the aqueous solution of HNO$_3$ or NaOH. Although it is difficult to evaluate only the mechanical effect of ultrasound without changing liquid properties in conventional ultrasound irradiation experiments, in this way, only the chemical effect of ultrasonic irradiation was mimicked so that the mechanical effect can be discussed simultaneously.

Before discussing the effects of the pH changes, we report some of the points we paid particular attention to in the titration procedure. Our preliminary experiment suggested that a higher concentration of the titrants (HNO$_3$ and NaOH) and faster titration speed lead to a larger deviation in both PTA and zeta potential measurements. Therefore, pH titration was performed under the following conditions: titration speed of ~ 10 μL s$^{-1}$ with 0.01 M HNO$_3$ or NaOH, and agitation of the sample at ~ 300 rpm. The gentle manipulations prevented the foaming and undesirable abrupt changes in pH and gave relatively low variability of data as will be discussed.

Fig. 8 shows the effect of pH on the zeta potential of UFBs. Each plot represents an independent titration. The top and bottom ends of the error bars in each plot indicate the maximum and minimum values of the concentration (DO) remained constant. The longer the irradiation time, the more NO$_3^-$ was produced. On the other hand, NO$_2^-$ was hardly produced; the concentration of NO$_2^-$ was almost the same as the detection limit of the water test. These experimental results confirmed that the formation of HNO$_3$ decreased pH and increased EC. Note that the liquid temperature shown in Table 1 was measured simultaneously with DO by the DO meter and therefore does not reflect the increase in liquid temperature caused by ultrasound irradiation.

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### Table 1

Time variation of nitrate ion, nitric ion and dissolved oxygen concentration and liquid temperature of pure water under ultrasonic irradiation.

| Irradiation time [min] | Concentration [mg L$^{-1}$] | Temperature [°C] |
|------------------------|-----------------------------|------------------|
|                        | NO$_3^-$ | NO$_2^-$ | DO |
| 0.5                    | 5        | 0.5      | 8.13 | 26.0 |
| 1                      | 20       | 1        | 8.34 | 26.2 |
| 5                      | 25       | N/A      | 8.26 | 25.8 |
| 15                     | 50       | 1        | 8.07 | 24.2 |
| 30                     | 100      | 1        | 8.58 | 25.3 |

Fig. 8. Effect of pH on the zeta potential of UFBs.

Fig. 9. Effect of pH on the stability of UFBs: the number concentration of (a) UFB-M and (b) UFB-G; the size of (c) UFB-M and (d) UFB-G.
The change in pH alone was not able to reduce the number concentration of UFBs to the same degree (Fig. 6b) since the addition of surfactant did not significantly destabilize the UFBs. Studies on the secondary Bjerknes force are limited to bubbles that are 10 μm or larger [43]. Therefore, no further quantitative discussion is possible in this study.

### 3.4. Destabilization of UFBs in a surfactant solution

Surfactants are known to have a significant influence on the stability of colloidal particles [35,44]. It has been reported that the addition of surfactants affects UFB stability [36,45,46]. Recently, Nirmalkar et al. [37] have studied the effect of the addition of three types of surfactant (nonionic, anionic, and cationic). They reported that nonionic surfactants have no significant effect on the zeta potential and do not destabilize UFBs, while anionic and cationic surfactants have a definite effect on the stability of UFBs, depending on the amount added. Therefore, in this study, polyethylene glycol monocetyl ether, a nonionic surfactant, was selected and added to the UFB dispersions. The UFB dispersions were previously prepared and the surfactant was added thereto. The concentration of the surfactant was 17.0 mg L\(^{-1}\), which is equivalent to 10 mg L\(^{-1}\) in TOC concentration.

Fig. 10 shows the effect of ultrasonic irradiation on the size distribution of UFBs in the nonionic surfactant solution. The comparison between Figs. 3 and 10 at 0 min, i.e., before irradiation, illustrates that the addition of the surfactant did not significantly destabilize the UFBs. This is consistent with the literature [37]. As is seen in Fig. 10, the ultrasonic irradiation destabilized the UFBs in the surfactant solutions; the peak at 90 nm in UFB-M and the peak at 150 nm in UFB-G decreased significantly with increasing irradiation time. Interestingly, the peak shift as seen in Fig. 3b was not found; instead, the number concentration of UFBs decreased rapidly. As a result of the absence of the peak shift, a sharp decline in number concentration can be seen for both UFB dispersion, as shown in Fig. 11. Regardless of the UFB generation method, more than 80% of the initial concentration of UFBs disappeared after 5 min of ultrasound irradiation. Based on the results, we conclude that this ultrasound irradiation method is also effective in destabilizing UFBs in nonionic surfactant solutions.

### 3.5. Selective destabilization of UFBs from the mixtures of polystyrene beads and UFB dispersions

As a step towards developing a method to distinguish UFBs from solid particles, UFBs were destabilized in a mixture of polystyrene latex (PSL) beads. The mixture consisted of UFB-G and PSL beads with a nominal diameter of 300 nm (3300A, Thermo Fisher Scientific, US). Note that PSL beads in a neutral liquid have a negative zeta potential of approximately −50 mV due to the sulfate groups located on the surface of the beads [47] and are therefore more stable than UFBs.
Fig. 12 shows the effect of ultrasonic irradiation on the stability of UFBs in the mixture with polystyrene beads. As is expected, the mixture showed a bimodal size distribution. The peak below approximately 200 nm represents UFB-G, whereas the peak around 250 nm represents the PSL beads. As the ultrasonic irradiation time increased, the peak representing UFBs became smaller and finally disappeared. Since PTA is still under development, especially in the case of multimodal samples, the difference between the nominal diameter of 300 nm and the measured peak diameter of 250 nm for PSL beads is considered acceptable [48].

The disappearance of UFBs can be seen in the 3D histograms as shown in Fig. 13, indicating that the ultrasonic irradiation destabilized UFBs without losing the stability of PSL beads. UFBs in this mixture disappeared as observed in Figs. 3b and 5c,d; larger UFBs having a peak diameter around 150 nm disappeared first, and then smaller UFBs disappeared. These results indicate that the ultrasonic irradiation method can selectively destabilize UFBs in the mixture with PSL beads, which have large absolute values of zeta potential and high dispersion stability.

Besides the main theme of the destabilization of UFBs, this study shows the potential of the analysis of using the raw data obtained by the PTA instrument (NanoSight) in quantitatively discussing the scattering intensity of particles. Therefore, we will briefly discuss the limitation of the scattering intensity measurement. Comparing Figs. 5c and 13a, the scattering intensities showing UFB-G appear to be slightly different; the peaks of UFB-G in Fig. 13a show higher scattering intensities than those in Fig. 5c. This does not mean that the scattering intensity of UFBs itself increased, but rather that the measured apparent scattering intensity distribution was affected by the presence of the PSL beads. For simplicity, if we assume the Rayleigh scattering regime, the scattering intensity is proportional to the sixth power of the particle size, as shown in Eq (3). According to this assumption, 300-nm PSL beads are roughly estimated to have a scattering intensity several hundred times stronger than 100-nm UFBs. When there is such a large difference in scattering intensity, the gain value of the camera, i.e., camera level for the NanoSight system, needs to be adjusted to the particles having the highest scattering intensity. Otherwise, very strong scattering light will be captured, which will seriously interfere with image analysis. Such a setting of the camera gain (camera level) for particles with high scattering intensity reduces the detection sensitivity of small particles, i.e., those with relatively low scattering intensity. For this reason, the PTA instrument may have underestimated the presence of smaller UFBs with low scattering intensities. Therefore, the measurement of particles with different refractive indices and/or broad size distributions is not as simple as the measurement of standard particles such as PSL beads. Improving the accuracy of PTA measurements for UFBs is one of the major challenges in the future.

4. Conclusions

We proposed a method to destabilize ultrafine bubbles (UFBs) using indirect ultrasonic irradiation. The frequency and power were 1.6 MHz and 30 W, respectively. UFBs were generated by two different types of
generators: the pressurized dissolution method and the swirling liquid flow method. Regardless of the UFB generation method, UFBs in pure water were destabilized by ultrasound irradiation and decreased to less than 10% of the initial concentrations after 30 min of irradiation. We measured the zeta potential and electrochemical properties of the liquid phase and proposed the following destabilization mechanism:

(i) Nitrogen oxides, mainly nitrate ion, NO₃, are formed by ultrasonic irradiation;
(ii) The formation of NO₃ decreases the pH and increases electrical conductivity;
(iii) Because of the change in the electrochemical properties, the zeta potential of UFBs approaches 0 mV, and their colloidal stability is lost.

In order to separately evaluate the chemical effects and the mechanical effects (e.g., the secondary Bjerknes force), only the pH was changed by titration. The experiment showed that not only the chemical effect caused by the above-mentioned mechanism but also the mechanical effect of ultrasound contributes to the destabilization of UFBs.

A feasibility study was conducted for UFBs in an aqueous surfactant solution and in a solid particle dispersion, respectively. The indirect mechanical effect of ultrasound contributes to the destabilization of UFBs.

Appendix A. Supplementary data

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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