

Zeta-potential of Micro- and/or Nano-bubbles in Water Produced by Some Kinds of Gases

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Abstract: Several reports in the literature show the acceleration in the physiological activity in plants and shellfishes when water containing micro- and nano-bubbles was used. However, the mechanisms of the phenomenon relating to aqua and agricultural fields and the stability of micro- and nano-bubbles in water have not been explained scientifically yet. The reason is the lack of knowledge about the characteristics of water containing micro- and nano-bubbles. In order to understand these characteristics, ζ -potential measurements were done in water after the generation of micro- and nano-bubbles using different kinds of gases. The values of ζ -potential were all negative and the absolute values were in the range between 34-45 mV (oxygen), 17-20 mV (air), 29-35 mV (nitrogen), 20-27 mV (carbon dioxide), and 11-22 mV (xenon). The different absolute values of ζ -potential may indicate different stability of the nano-bubbles according to the type of gas, as well as different structures at the gas-liquid interface. Furthermore, the bubbling time seemed to affect the ζ -potential, but more studies are needed to understand the phenomena during the production of micro- and nano-bubbles.

Keywords: Bubbles, Micro-bubble, Nano-bubble, Zeta-potential, Bubble Stability, Water

1. INTRODUCTION

Micro- and nano-bubbles (MNB) have diameter smaller than several tens of micrometers. At this small size, bubbles are supposed to present different physicochemical and fluid dynamic properties than ordinary macro-bubbles (Serizawa et al. 2003).

Among the physicochemical characteristics of MNB, there is the large specific area and the high pressurization of gas inside the bubble, which confer to these bubbles high gas dissolution capability (Bredwell and Worden 1998). Furthermore, MNB were reported to have an electrically charged surface (Takahashi 2005; Ushikubo et al. 2010). It was also observed free-radical generation with the micro-bubble collapse (Takahashi et al. 2007). In addition, Fan et al. (2004) reported that air micro-bubbles were pseudo-elastic and spherical in aqueous solutions. Regarding the fluid dynamic properties, it was cited the low rising velocity under the liquid phase and the reducing frictional resistance (Tsuge 2007). Besides these characteristics, it is supposed that there are still some other unknown properties of MNB.

Successful applications of MNB in aqua and agricultural have been reported. The use of MNB in these fields aims to improve the aeration in aquacultures, to promote the acceleration of physiological activity in the living organisms and the disinfection of the products (Endo et al. 2008).

The air micro-bubble supply in the cultivation of oysters resulted in a better quality product in terms of size and taste

(Onari 2001). In the hydroponic cultivation of lettuce using air micro-bubbles, Park and Kurata (2009) observed an increase in growth of leaves in a ratio 2.1 times larger than a lettuce grown without micro-bubbles. In addition, Endo et al. (2008) showed the application of micro-bubbles in fish farm. With the generation of MNB, the dissolved oxygen concentration of the sea increased, improving the water quality. Moreover, it was observed an increase in the growth of colonies of *Saccharomyces cerevisiae* with the use of air MNB (Himuro et al. 2009). On the other hand, in this same study, the authors observed an antimicrobial activity caused by the MNB in *Escherichia Coli*, *Salmonella typhimurium*, *Staphylococcus aureus* and *Bacillus subtilis*. Tsuge et al. (2009) also reported the efficiency of ozone micro-bubbles in inactivating microorganisms.

However, the mechanism of the acceleration of the physiological activity by the MNB has not been elucidated yet. The main obstacle is to understand the characteristics of the water containing MNB.

One of the important properties of MNB is the electrical charges on the bubble surface. The low electrical potential created by the charged surfaces of MNB could be related to the physiological activation in living organisms (Serizawa et al. 2003).

The electrical potential of a particle in a colloidal system can be expressed by the ζ -potential. The ζ -potential is defined as the electrical potential at the slipping plane of a particle. The slipping plane is the boundary layer that divides the double

layer formed by the counter ions on the particle and the bulk solution (Malvern 2003-2004).

Many reports in the literature discuss about the difficulty of measuring the ζ -potential in a dispersion of bubbles because of the interference of the gravitational field and of the lack of stability of the bubbles during the measurements (Graciaa et al. 2002). In the case of MNB, the long residence time in the liquid due to the low rising velocity of the bubble is an advantage in the ζ -potential measurement (Takahashi 2005).

In this study, the ζ -potential of MNB produced with different kind of gases was measured. The aim was to understand the influence of the type of gas in the MNB surface charge.

2. MATERIALS AND METHODS

2.1 Materials

Micro- and nano-bubbles were produced in commercial ultrapure water (Kanto Chemical Co. Inc., Japan). The high level of purity of the water is important to ensure that the ζ -potential measured in the water was not affected by ions or impurities.

The gases used to generate the micro- and nano-bubbles were oxygen (99.999%, Nissan Tanaka Co., Japan), nitrogen (99.9995%, Nissan Tanaka Co., Japan), carbon dioxide (99.995%, Nissan Tanaka Co., Japan), xenon (99.995%, Iwatani Sangyo Co. Ltd., Japan) and air. The air was suctioned from the atmosphere, passing through a filter in the gas inlet.

2.2 Micro-bubble Generation

The micro- and nano-bubbles were generated using a method that combines the high shear force of the pump to mix water and gas, and the gas nucleation created by the rapid pressure drop.

The micro-bubble generator (OM4-GP-040, Aura Tec Co. Ltd., Japan) is composed by a magnetic gear pump (MDG-R2RVA100, Iwaki Co. Ltd., Japan), a pressurized tank (0.25 to 0.27 MPa) and a nozzle (ejector type) in the outlet.

The volume of water was set to 2 L, the gas flow rate was 0.1 NL·min⁻¹ (20°C, 0.101 MPa) and the temperature of the water was controlled using a water bath (NTT-1300, Tokyo Rikakikai Co. Ltd., Japan) at 20°C. The water was circulated in the micro-bubble generator for 30 minutes. The water obtained after the generation of micro- and nano-bubbles will be referred to as “MNB water” in this study.

2.3 ζ -potential Measurements

ζ -potential (zeta-potential) was measured by a Zeta Potential Analyzer (Zeecom, Microtech Co. Ltd., Japan). This analyzer is equipped with a CCD camera and an optical microscope that can detect the electrophoretic mobility of particles when a voltage is applied. The sample was analyzed in a 1 mm ×

10 mm glass cell. The particles are detected in the range from 20 nm to 100 μ m by the scattering of halogen light or laser. The voltage was set to 30 V and the distance between the electrodes was 9 cm. Fifty particles were tracked manually to determine their speed. The ζ -potential was calculated using Smoluchowski Equation:

$$\zeta = \frac{4\pi\eta}{\varepsilon} U, \quad (1)$$

in which ζ is the ζ -potential (V), η is the viscosity of the medium (Pa·s), ε is the permittivity of the medium (F·m⁻¹) and U is the electrophoretic mobility ((m/s)·(V/m)⁻¹). U is defined by:

$$U = \frac{v}{V/L}, \quad (2)$$

in which v is the particle speed (m·s⁻¹), V is the voltage applied (V) and L is the distance of the electrodes (m).

The measurements of ζ -potential were performed on the first hours after the bubble generation and on the following days. The samples were stored in a room at constant temperature of 20°C.

In addition, the bubbling time effect on the ζ -potential was tested. The ζ -potential was measured at 30, 90, 120 and 150 minutes of MNB generation.

2.4 DO Concentration and pH Measurements

The dissolved oxygen (DO) concentration was determined using a high performance DO meter (SG6, Mettler-Toledo GmbH, Switzerland), which detects oxygen concentration from 0 to 99 mg·L⁻¹. The measurements of DO concentration were done at 20°C.

The pH was measured by a pH meter (D-55, Horiba Ltd., Japan). The pH meter was set to adjust automatically the values at 20°C.

3. RESULTS AND DISCUSSION

3.1 Image of optical microscope

The image obtained of the O₂ MNB water observed through the optical microscope of the Zeta Potential Analyzer is shown in Fig. 1. The particles observed in the images have diameter smaller than 10 μ m. However, they are not in the real scale, but they were scattered by a laser source.

For the reason of comparison, images of polystyrene dispersions with particle size previously known (200 nm and 350 nm diameter) are also shown. These samples were observed in the same condition as the O₂ MNB water.

Since the particles of the O₂ MNB water seem to have size between the particle sizes of the two polystyrene dispersions, it is supposed that their real size is in the same range. However, it is important to observe that this is just an

estimative, since the refraction indexes of polystyrene (1.59-1.60; Mark 1998) and oxygen (near 1.00) are different.

The particles observed in the O₂ MNB water image are supposed to be nano-bubbles that were scattered by the laser source. This interpretation is based on a previous study, in which the measurement of the particle size distribution through dynamic light scattering method indicated the presence of nano-bubbles of a few hundreds nanometers in the water after the generation of MNB (Ushikubo et al. 2010).

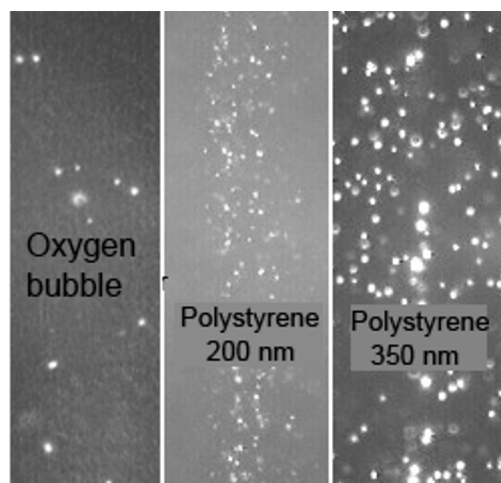


Fig. 1 Image of O₂ MNB water, dispersion of 200 and 350 nm diameter polystyrene observed through optical microscope with the scattering of laser

The scattered bubbles moved with the application of a voltage. This fact showed that the nano-bubbles are electrically charged, as many studies suggest.

In addition, the observation of the scattered bubbles could give a qualitative estimative of the amount of nano-bubbles in the water. In the first hours after the generation of MNB in the water, many moving particles of laser scattering were observed through the microscope, while after some days, the number density of particles decreased.

3.2 ζ -potential measurements

The ζ -potential measured in water after the generation of MNB using different kind of gases is presented in Fig. 2. It can be noticed that all the values were negative. The negative ζ -potential in bubble dispersions indicates that there is preferential adsorption of OH⁻ at the bubble interface, as already discussed in many studies (Graciaa et al. 2002; Usui and Sasaki 1978).

Although all values were negative, differences were found between the samples. O₂ and N₂ MNB presented higher absolute ζ -potential (34-45 mV and 29-35, respectively), while the measurements of ζ -potential in air, CO₂ and Xe MNB samples resulted in lower absolute values (17-20 mV, 20-27 mV and 11-22 mV, respectively).

The ζ -potential values reported in the literature varied widely: Usui and Sasaki (1978) obtained an average value of -15 mV

in distilled water with argon bubbles and Graciaa et al. (1995) reported a ζ -potential of -65 mV in deionised water with air bubbles.

Furthermore, it could be observed in Fig. 2 that the values of ζ -potential presented only small fluctuations with time. That is, there was no general tendency of increasing or decreasing in ζ -potential. Although the ζ -potential practically did not change, the images of the samples observed through the optical microscope showed a decrease in the number density of scattered particles with time (qualitative data). Therefore, the ζ -potential is not related to the number density of bubbles in the water, but to the charge of the bubble itself.

The magnitude of ζ -potential indicates the stability of a colloidal system. The DLVO (Deryaguin-Landau-Verwey-Overbeek) theory states that the balance between the attractive Van der Waals forces and the repulsive electrical forces due to the surface charge is decisive for the stability of colloids. The minimum absolute value of 30 mV is generally considered to judge an aqueous dispersion as stable (Spanos et al. 2002).

In the case of bubble dispersions, the high negative ζ -potential of MNB was related to the stability of bubbles (Ushikubo et al. 2010). The authors observed that the detection of nano-bubbles by dynamic laser scattering method in O₂ MNB water lasted from 3 to 15 days, depending on the initial DO concentration, while the presence of nano-bubbles in air MNB water could be detected for less than one hour. The high absolute ζ -potential measured in O₂ MNB water could avoid the coalescence of bubbles and, therefore, contribute to the stability of the nano-bubbles.

In addition, the electrical charge could indicate a different hydrogen-bonding network at the gas-liquid interface from that of the bulk water (Takahashi 2005).

Thus, the change of the ζ -potential values found with the kind of gases may indicate different structures at the interface and the nano-bubbles might have different stability according to the type of gas.

Regarding the DO concentration, it was observed a high value in the O₂ MNB water (40.8 mg·L⁻¹), characterizing a supersaturation condition with time. The DO concentration decreased with time until reach the saturation equilibrium (9.1 mg·L⁻¹ at 20°C) on the third day after the bubble generation. The air MNB water presented initial DO concentration of 10.7 mg·L⁻¹. After 2 h, the value decrease to 9.5 mg·L⁻¹ and on the next measurement, 1 day after the bubble generation, the DO concentration was 9.0 mg·L⁻¹. It is interesting to observe that, although the saturation equilibrium of the dissolved oxygen was reached, the ζ -potential was kept practically stable.

In the samples with N₂, CO₂ and Xe, the DO concentration became lower (0.8, 0.8 and 0.2 mg·L⁻¹, respectively) because of the release of oxygen from the water. The DO concentration increased with time towards the saturation equilibrium.

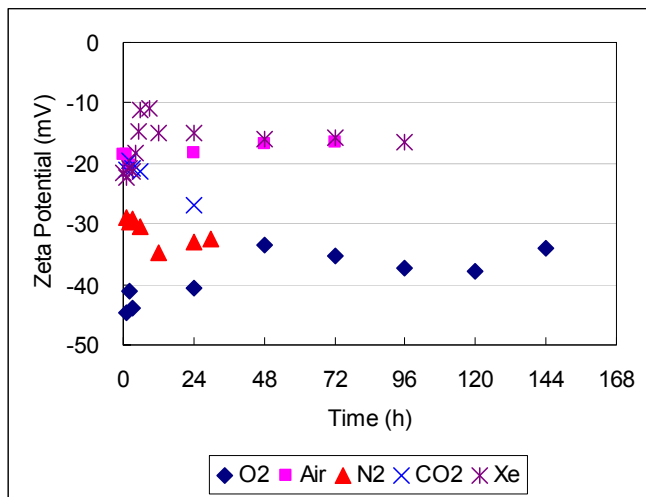


Fig. 2 ζ -potential of the water after the generation of O₂, air, N₂, CO₂, and Xe MNB in water

The pH of the samples of MNB water is shown in Fig. 3. While most of the gas had pH in the range between 6.1 and 6.4, the CO₂ MNB water presented pH around 4.0 because of the increase of H⁺ originated from the dissolution of CO₂ in water:

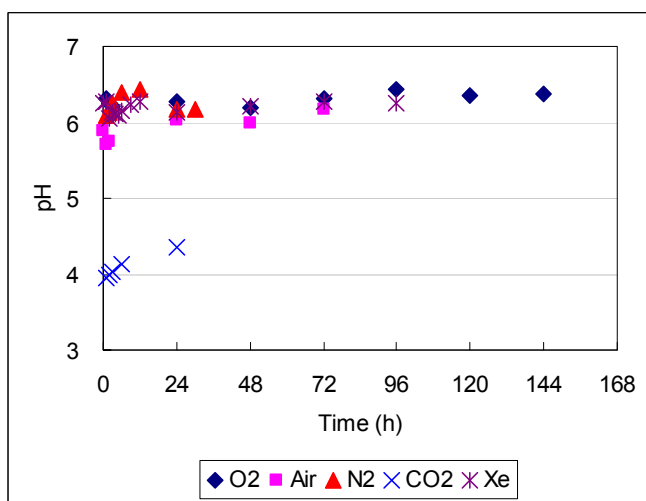


Fig. 3 pH of the water after the generation of O₂, air, N₂, CO₂, and Xe MNB in water

Moreover, since the air also contains a small portion of CO₂, the value of pH was slightly smaller than the other gases, around 5.7. This value increased to 6.2 after 3 days.

The change in pH can affect the ζ -potential of the samples. Many studies indicate that, in an aqueous solution with air bubbles, the isoelectric point is in the range between 2 and 3 (Brandon and Kelsall 1985; Najafi et al. 2007). That is, at pH > 3, the bubbles were negatively charged, while at pH < 2, the bubbles became positive. Hasegawa et al. (2008) has observed negative ζ -potential in aqueous solution at pH 4, 6.8 and 10. At lower pH, the absolute value of ζ -potential was lower. Thus, the lower absolute value of ζ -potential observed in the CO₂ MNB water could be related to the low pH.

On the other hand, in the case of the air MNB, the difference in pH is too small to cause such a big change in the ζ -potential. In addition, the Xe MNB water presented pH similar to gases such as oxygen and nitrogen, but presented a much lower ζ -potential absolute value. Therefore, the reason for the different ζ -potential among the different gases is not only the pH.

The kind of gas may contribute for the structure of the bubble. Graciaa et al. (2002), in a review of electrokinetics of bubbles, concluded that the vapour pressure inside the bubbles is not enough to modify the structure at the interface. Therefore, the gas would not play a role in the structure of the bubble surface. However, the same authors said that, if the size of bubbles is reduced significantly, the gas could affect the interface. Thus, in the case of nano-bubbles, the kind of gas may have an important role in the interface structure.

Properties such as the solubility and density of gases are important to evaluate the structure and stability of bubbles. Table 1 shows the properties of the gases used in this study. The solubility of the xenon gas is 3.6 times higher than that of the oxygen and 7.1 times higher than that of the nitrogen. In addition, the density of xenon is much higher than that of oxygen and nitrogen. The different properties of xenon in relation to the other gases could result in different characteristics of xenon bubbles.

For example, higher solubility of the gas results in larger bubbles. Haedelt et al. (2007) used gases with different solubility (N₂O, CO₂, Ar, N₂) to produce aerated chocolate and observed the structures by X-ray tomography. The gases with higher solubility (N₂O and CO₂) produced bubbles of larger diameter than those of lower solubility.

Table 1. Solubility in water and density of different gases (Source: Lide, 1995-1996)

Gas	Solubility at 293.15 K, 101.3 kPa (10 ⁵ mol gas/mol H ₂ O)	Density at 298.15 K, 101.3 kPa (kg/m ³)
O ₂	2.501	1.404
N ₂	1.274	1.229
CO ₂	70.07	1.931
Xe	9.051	5.761

3.3 Bubbling time effect

The bubbling time effect on the ζ -potential was verified and the results are shown in Fig. 4. With the increasing bubbling time from 30 to 90 min, the absolute value of ζ -potential decreased from 45 to 33 mV. However, after 90 min, the ζ -potential did not change significantly.

The DO concentration was 40.8 mg·L⁻¹ at 30 min, 36.4 mg·L⁻¹ at 90 min, 37.4 mg·L⁻¹ at 120 min and 33.8 mg·L⁻¹ at 150 min. The pH was practically constant: 6.3 at 30 min and 6.5 at 90, 120 and 150 min.

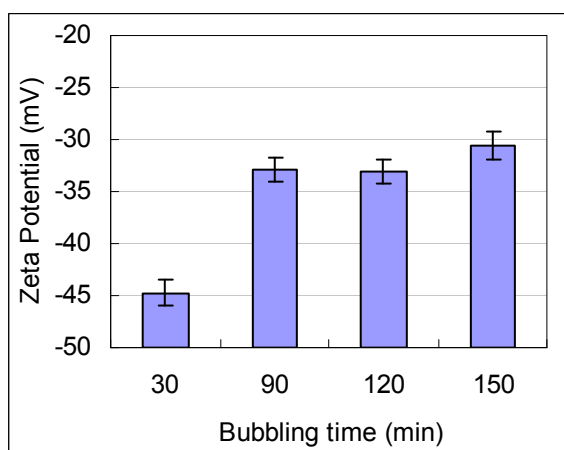


Fig. 4 ζ -potential of O₂ MNB water at different bubbling times.

Although there is a clear difference between the first and the following measurements, it is difficult to say if the difference was caused by the bubbling time or if that was only a fluctuation of results. As shown in Fig. 2, the ζ -potential of O₂ MNB water fluctuated between -45 mV to -34 mV during the observation time. The lowest absolute value is near of that obtained at 90 and 120 min of bubbling (-33 mV).

With the increase of the bubbling time, it was expected that the number density of bubbles would increase. A slight increase in the number of bubbles was observed in the images obtained through the optical microscope. It is also expected that the properties of water would change with the bubbling time. This possibility will be investigated in the future study.

4. CONCLUSIONS

The images obtained through the optical microscope with the scattering laser showed particles in the range of few hundreds of nanometers. These particles moved with the application of a voltage, indicating that they are electrically charged. The ζ -potential of the water after the generation of micro- and nano-bubbles was negative in all samples, but the values varied with the kind of gas. Higher absolute ζ -potential were obtained in O₂ and N₂ MNB waters, while air, CO₂ and Xe showed lower absolute values. The difference in ζ -potential could indicate different bubble stability. The causes for the different ζ -potential values with different kind of gases are still not clear, but the gas should play a role in the bubble structure at nano-scale. Finally, the bubbling time seems to affect the ζ -potential in the O₂ MNB water, although a more detailed investigation should be done to clarify this point.

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REFERENCES

- Brandon, N.P., Kelsall, G.H. (1985). Interfacial electrical properties of electrogenerated bubbles. *Journal of Applied Electrochemistry* 15, 485-493.
- Bredwell, M.D. and Worden, R.M. (1998). Mass-transfer properties of microbubbles. 1. experimental studies. *Biotechnology Progress*, 14(1), 31-38.
- Endo, A., Srithongouthai, S., Nashiki, H., Teshiba, I., Iwasaki, T., Hama, D., Tsutsumi, H. (2008). DO-increasing effects of a microscopic bubble generating system in a fish farm. *Marine Pollution Bulletin*, 54(1-5), 78-85.
- Fan, X., Zhang, Z., Li, G., Rowson, N.A. (2004). Attachment of solid particles to air bubbles in surfactant-free aqueous solutions. *Chemical Engineering Science*, 59(13), 2639-2645.
- Graciaa, A., Morel, G., Saulner, P., Lachaise, J., Schechter, R.S. (1995). The ζ -potential of gas bubbles. *Journal of Colloid and Interface Science*, 172, 131-136.
- Graciaa, A., Creux, P., Lachaise, J. (2002). Electrokinetics of bubbles. In Hubbard, A.T. (ed.) *Encyclopedia of Surface and Colloid Science*, 829-845. Marcel Dekker, New York.
- Haedelt, J., Beckett, S.T., Niranjan, K. (2007). Bubble-included chocolate: relating structure with sensory response. *Journal of Food Science*, 72(3), E138-E142.
- Hasegawa, H., Nagasaka, Y., Kataoka, H. (2008). Electrical potential of microbubble generated by shear flow in pipe with slits. *Fluid Dynamics Research*, 40(7), 554-564.
- Himuro, S., Deguchi, T., Takamatsu, R. (2009). Effects of microbubbles on bacteria. *Progress in Multiphase Flow Research*, 4, 95-102.
- Lide, D.R. (ed.) (1995-1996). *Handbook of Chemistry and Physics*. 79th ed., CRC Press, Boca Raton.
- Malvern (2003-2004). *Zetasizer Nano Series User Manual*. Malvern Instruments Ltd., Worcestershire.
- Mark, J. E. (ed.) (1998). *Polymer Data Handbook*. Oxford University Press, New York.
- Najafi, A.S., Drelich, J., Yeung, A., Xu, Z., Masliyah, J. (2007). A novel method of measuring electrophoretic mobility of gas bubbles. *Journal of Colloid and Interface Science*, 308(2), 344-350.
- Onari, H. (2001). Fisheries Experiments of cultivated shells using micro-bubble techniques. *Journal of Heat Transfer Society of Japan*, 40(160), 2-7. (in Japanese)
- Park, J. and Kurata, K. (2009). Application of microbubbles to hydroponics solution promotes lettuce growth. *Hort Technology*, 19(1), 212-215.
- Serizawa, A., Inui, T., Yahiro, T., Kawara, Z. (2003). Laminarization of micro-bubble containing milky bubbly flow in a pipe. In *Proceedings of the 3rd European-Japanese Two-Phase Flow Group Meeting*, 21-27 September, 2003. Certosa di Pontignano.
- Spanos, N., Klepetsanis, P.G., Koutsoukos, P.G. (2002). Calculation of zeta-potentials from electrokinetic data. In Hubbard, A.t. (ed.) *Encyclopedia of Surface and Colloid Science*, 829-845. Marcel Dekker, New York.
- Takahashi, M. (2005). ζ potential of microbubbles in aqueous solutions: electrical properties of the gas-water interface. *Journal of Physical Chemistry B*, 190(46), 21858-21864.

- Takahashi, M., Chiba, K., Li, P. (2007). Free-radical generation from collapsing microbubbles in the absence of a dynamic stimulus. *The Journal of Physical Chemistry B*, 111(6), 1343-1347.
- Tsuge, H. (2007). *The latest technology on microbubbles and nanobubbles*, chapter 1, 1-14. CMC, Tokyo. (in Japanese)
- Tsuge, H., Li, P., Shimatani, N., Shimamura, Y., Nakata, H., Ohira, M. (2009). Fundamental study on disinfection effect of microbubbles. *Kagaku Kogaku Ronbunshu*, 35(5), 548-552.
- Ushikubo, F.Y., Furukawa, T., Nakagawa, R., Enari, M., Makino, Y., Kawagoe, Y., Shiina, T., Oshita, S. (2010). Evidence of the existence and the stability of nanobubbles in water. *Colloids Surf. A: Physicochem. Eng. Aspects*, Volume 361, Issues 1-3, 31-37
- Usui, S. and Sasaki, H. (1978). Zeta potential measurements of bubbles in aqueous surfactant solutions. *Journal of Colloid and Interface Science*, 65(1), 36-45.