Partial Quenching of Sonoluminescence by Monoatomic Gases

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In a solitary bubble trapped at the antinode of the standing acoustic field in water, the density increase of *n*-butanoic acid in the bubble quenched the sonoluminescence in consuming the acoustic energy by sonochemical reaction. In the bubbles filled with inert gases (He, Ar, and Xe), the quenching was obvious in Xe, but in He. These observations suggest that He locating at the bubble center reduces the sonochemical reactivity.

Liquids irradiated by ultrasound undergo the acoustic cavitations.[1] Formed bubbles repeat the growth and the collapse cycles during the rarefaction and the compression phase of the acoustic field, respectively. In the violent collapse, the energy charged in the growth cycle is released as acoustic noise, shock wave, chemical reaction, and/or light emission. A hot spot is created at the center of the collapsing bubble, where a sonochemical reaction proceeds.

The sonochemical reactivity is known to be dependent on the atmospheric inert gas, which saturates in water. In the series of the inert gases, the sonochemical reactivity follows the order He < Ne < Ar < Kr < Xe.[2,3] Since the polytropic index is the same; $C_p/C_v = 1.67$ for monoatomic gas, the reactivity is believed to be governed by the thermal conductivities of the gases.[4] The lower thermal conductivity results in the higher temperature and consequently the higher reactivity. However, here we found the molecular weight of the atmospheric gas is an additional parameter critical for the sonochemical reactivity.

A solitary bubble was trapped at the center of a spherical cavity filled with degassed water, if necessary containing 67 μM of *n*-butanoic acid, under the standing acoustic field with a frequency of 51.6 kHz.[5] The bubble was successfully trapped, once touching the liquid surface by a needle.

Temporal change in the bubble size, the profile of the bubble diameter and time i.e., $R(t)$ curves were collected by strobe method using a nanosecond flash light (Xe Corp. Nanopulser 437, FWHM = 5 ns). Temporal change in $R(t)$ was shown in Figure 1. The bubble breathing motion was asymmetric. The bubble collapses very rapidly, where the quasi-adiabatic implosion proceeds and the temperature increases in the bubble. In the presence of *n*-butanoic acid, the maximum size of the bubble enlarged about 10%; R_{max}'s were 60 and 70 μm in pure water and in aqueous solution containing 67 μM of *n*-butanoic acid, respectively. This suggests the adsorption of the molecule at the bubble wall, i.e., the gas and liquid interface, reduced the surface tension.

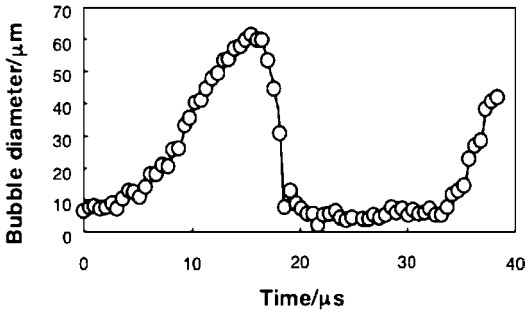

Figure 1. Temporal change in the bubble size in pure water obtained by the strobe method.

The sonoluminescence spectra were obtained by a spectrometer (Acton, SP-150) combined with a CCD camera (Princeton instrument, PI-Max512UV). The spectra were obtained under gently flowing rare gas over the cavity after at least one-hour continuous flow. Sonoluminescence spectra in pure water were constant for more than 3 h. When pH of pure (without *n*-butanoic acid) water was varied by adding NaOH or HCl, no substantial change was observed in neither the spectra nor in the bubble dynamics.

With *n*-butanoic acid in the solution, the density of the molecule in the bubble can be controlled by pH, since the molecules are volatile into the bubble only in their neutral form as reported by Ashokkumar et al.,[6,7]

$$CH_3(CH_2)_2COOH + H_2O \rightleftharpoons H_3O^+ + CH_3(CH_2)_2COO^-$$
$$pK_a = 4.8$$

In the solution containing 67 μM of *n*-butanoic acid, the luminescence spectra were obtained under atmospheres of the rare gases. The spectra of Xe-seeded bubble under Xe atmosphere were shown in Figure 2a at several pH. At pH over 6, the intensity was constant and identical to that obtained without *n*-butanoic acid, whereas it decreased as pH decreases below 6. In the acidic region, the spectral shape was broadened and also the peak wavelength was red-shifted. In this region, in the Xe bubble, the reaction of water and *n*-butanoic acid at high temperature will produce hydrocarbons. The charged energy by the implosion is consumed by this sonochemical reaction, and the sonoluminescence is partially quenched. However, in the case of He-seeded bubble under He atmosphere, Figure 2b shows that the emission intensity and the spectral shape were independent of pH. The constant emission spectra in the He bubble demonstrate that the sonochemical reaction cannot proceed even in the presence of the neutral form of *n*-butanoic acid in the bubble (pH < 6). In the case of Ar bubble, the pH effect was quite obvious in the emission intensity but not in the peak shift. All of the spectra were different from those expected by the black body radiation. For the comparison of the pH responses for He, Ar, and Xe bubbles, the pH dependence of the intensity and the peak wavelength were plotted in Figures S1a and S1b, respectively.[11] In Xe bubble, the distinct pH effects were observed, but Ar and He bubbles did not show the unambiguous change. The pH effect was increased in the series of He < Ar ≪ Xe.

The thermal conductivity of these inert gases is shown in Table 1. The conductivity decreases as increase in the molecular

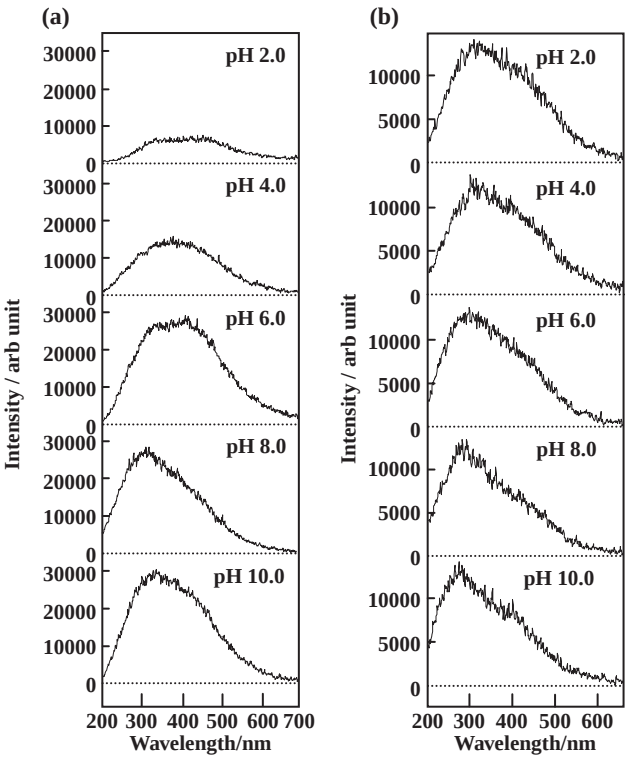

Figure 2. Emission spectra of Xe bubble (a) and He bubble (b) at different pH in the solution containing *n*-butanoic acid.

weight. Although the thermal conductivity of He is one order of magnitude larger than that of Ar, the gap of the quenching is between Ar and Xe. This suggests an additional control factor exists for determining the sonochemical reactivity.

Storey and Szeri,[8] and Yasui[9] suggested the spatial segregation of chemical species in the bubble, which is caused by the extreme temperature and pressure gradients in the sonoluminescing bubble. Their model calculations suggest that the heavier gas is driven to the wall and the lighter gas is driven to the bubble center, i.e., a hot spot. In our experiments, the molecular weight M of the gaseous species are M_{Xe} (131) > $M_{n\text{-butanoic acid}}$ (88) > M_{Ar} (40) > M_{water} (18) > M_{He} (4), where the numbers in parentheses are the corresponding molecular weights, it is only Xe that has the heavier molecular weight than those of *n*-butanoic acid and water. Thus, inside the Xe bubble, water and *n*-butanoic acid are driven to the bubble center, and Xe is exclusively driven to the wall. On the other hand, inside the He bubble, He is at the center, and water and *n*-butanoic acid are around the wall. In the acidic region, Xe surrounds the polyatomic molecules, water and *n*-butanoic acid, and sonochemical reaction proceeds at the central hot spot. But, in the Ar and He bubbles, since nonreactive noble gases locate at the center, the sonochemical reaction cannot proceed.

Table 1. Molecular weights and thermal conductivity of gases

Gas	Molecular weight	Thermal conductivity[4] mW/mK
He	4	151
Ar	40	17.9
Xe	131	5.62
n-Butanoic acid	88	—

Conclusively, although the thermal conductivity has been believed the critical contribution to the sonochemical reactivity, we have experimentally probed the additional contribution of the molecular segregation in the bubble proposed by Storey, Szeri, and Yasui.[8,9] In aqueous solution containing *n*-butanoic acid, in the bubble, Xe surrounds the polyatomic molecules, water and *n*-butanoic acid. But, in Ar and He bubbles, the nonreactive rare gases locate at the center. The emission spectra obtained in acidic and basic pH range can be well explained by the combination of the thermal conductivity and the molecular segregation in the bubble. Furthermore, these results potentially suggest that the Ar rectification,[5,10] if this process occurs under open-air conditions, decreases sonochemical reaction efficiency for the molecules whose molecular weights are lighter than that of Ar.

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11 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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