

## Sonoluminescence and Bubble Dynamics in Phosphoric Acid: Comparison with Those in Sulfuric Acid

リン酸中のソノルミネッセンスと気泡ダイナミクス: 硫酸との比較

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### 1. Introduction

Sonoluminescence (SL) is the phenomenon of light emission from acoustic cavitation bubbles at collapse, where acoustic energy is concentrated by 12 orders of magnitude to create flashes of light.<sup>1)</sup> Because liquid vapor may cushion the collapse and more energy may be consumed by endothermic bond dissociations of liquid vapor, SL in a variety of low-volatility liquids has been explored especially by Suslick and his colleagues. Then, Flannigan and Suslick have discovered extremely intense SL from a moving single-bubble cavitation in concentrated aqueous sulfuric acid ( $\text{H}_2\text{SO}_4$ ) solutions,<sup>2)</sup> which is a strongly hydrogen-bonded liquid with very low vapor pressure and relatively high viscosity. According to the paper, under optimal conditions, the SBSL intensity from 85 wt%  $\text{H}_2\text{SO}_4$  (aq.) under Ar can be increased 2,700 times compared to that from water under Ar, and the intensity under Xe can be increased 1,500 times compared to water under Xe. The extremely high brightness of SL in  $\text{H}_2\text{SO}_4$  suggested the study of similar liquids, of which aqueous phosphoric acid ( $\text{H}_3\text{PO}_4$ ) is the only common example. Then, Xu and Suslick have discovered extremely intense SL from a moving single bubble in 65 wt%  $\text{H}_3\text{PO}_4$  (aq.) with very strong molecular emission from excited OH radicals.<sup>3)</sup> They determined the very high vibrational temperatures of nearly 10,000 K by simulation of OH rovibrational spectra. On the other hand, the vibrational temperatures of 1,500 to 3,500 K were determined by simulation of SO in 85 wt%  $\text{H}_2\text{SO}_4$ .<sup>2)</sup> Since the vapor pressure of 65 wt%  $\text{H}_3\text{PO}_4$  (aq.) is two orders of magnitude higher than that of 85 wt%  $\text{H}_2\text{SO}_4$  (aq.), there might exist a dominant factor for ultrabright SL other than low vapor pressure of liquids.

In this study, SL and bubble dynamics in  $\text{H}_3\text{PO}_4$  during both single-bubble and multibubble cavitation are investigated, comparing with those in  $\text{H}_2\text{SO}_4$ . From the experimental results, possible mechanisms for ultrabright SL will be discussed.

### 2. Experimental

Experiments were carried out in aqueous

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solutions of  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{SO}_4$  with various concentrations. In multibubble case, a commercial ultrasonic horn apparatus at 20 kHz (Branson, Sonifier 450) was used. Spectra of MBSL were measured in the range from 200 to 850 nm using a spectroscope (Hamamatsu, C8801) through a quartz glass fiber. In single-bubble case, a rectangular quartz glass cell with a bolt-cramped Langevin-type transducer at the bottom was used. The dynamics of single-bubble cavitation was observed by laser-light scattering and stroboscopic observation method. The details of the method and the experimental setup is described elsewhere.<sup>4)</sup>

### 3. Results and Discussion

Figure 1 shows photographs of MBSL in 85 wt%  $\text{H}_3\text{PO}_4$  (aq.) under Xe for 10, 20 and 30  $\text{W}/\text{cm}^2$  in ultrasonic intensity by calorimetry in a well-lit room. The MBSL intensity in 85 wt%  $\text{H}_3\text{PO}_4$  (aq.) was higher than that in 95 wt%  $\text{H}_2\text{SO}_4$  (aq.), in spite of higher vapor pressure of  $10^{-2}$  Pa for 85 wt%  $\text{H}_3\text{PO}_4$  (aq.) than that of  $10^{-4}$  Pa for 95 wt%  $\text{H}_2\text{SO}_4$  (aq.). The corresponding MBSL spectra to the photographs in Fig. 1 are shown in Fig. 2. From spectral measurement, the MBSL intensity at 10  $\text{W}/\text{cm}^2$  in  $\text{H}_3\text{PO}_4$  was about 1.5 times higher than that in  $\text{H}_2\text{SO}_4$ , although the spectra is not shown.

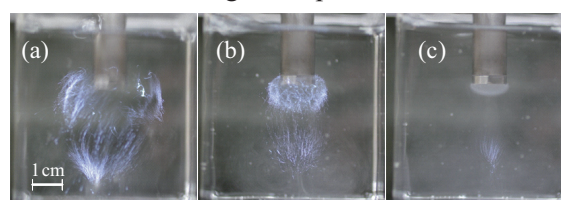


Fig. 1. MBSL photos in 85wt%  $\text{H}_3\text{PO}_4$  (aq.) under Xe for (a) 10, (b) 20, and (c) 30  $\text{W}/\text{cm}^2$ .

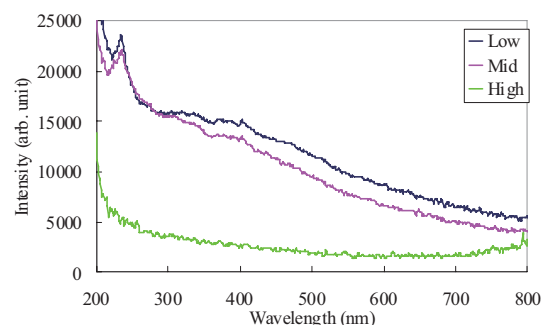


Fig. 2. Corresponding MBSL spectra in 85 wt%  $\text{H}_3\text{PO}_4$  (aq.) to the photos shown in Fig. 1.

**Figure 3** shows photographs of MBSL in 85 wt%  $\text{H}_3\text{PO}_4$  (aq.) and those in 95 wt%  $\text{H}_2\text{SO}_4$  (aq.) under Xe for 10, 20 and 30  $\text{W}/\text{cm}^2$  in the presence of 1 M sodium (Na) salt. The MBSL intensity in  $\text{H}_3\text{PO}_4$  decreased by dissolving  $\text{Na}_3\text{PO}_4$ , in contrast to that in  $\text{H}_2\text{SO}_4$ , which is remaining unchanged. The orange colored region of Na atom emission in  $\text{H}_3\text{PO}_4$  is narrower than that in  $\text{H}_2\text{SO}_4$ , where the filamentous structures of bubble streamers are not different between them. It is probably because the viscosity of 100 mPas for 85 wt%  $\text{H}_3\text{PO}_4$  at  $20^\circ\text{C}$  is higher than that of 26 mPas for 95 wt%  $\text{H}_2\text{SO}_4$ , where Na emission may require unstable bubble oscillation.<sup>5)</sup> The spectra in 1 M  $\text{Na}_3\text{PO}_4$ - $\text{H}_3\text{PO}_4$  aq. solution is shown in **Fig. 4**, where the emission of OH radicals is appeared. **Figure 5** shows the comparison between phosphoric and sulfuric acid solutions.

**Figure 6** shows radius-time curve of a sonoluminescence single-bubble in 35 and 55 wt%  $\text{H}_3\text{PO}_4$  (aq.) under Ar. The pulse intensity of SBSL in 35 wt%  $\text{H}_3\text{PO}_4$  was the almost same as that in water and is smaller than that in 55 wt%, where the computer simulation of SBSL intensity in 35 wt% has the maximum intensity because of viscosity.<sup>6)</sup>

#### 4. Conclusion

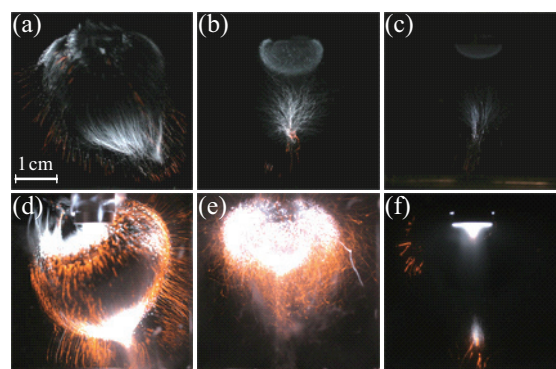
The spectral intensity of SL produced by an ultrasonic horn at 20 kHz in 85wt%  $\text{H}_3\text{PO}_4$  (aq.) was higher than that in 95wt%  $\text{H}_2\text{SO}_4$  (aq.), in spite of higher vapor pressure. In the presence of Na salt, the Na atom emission region of SL in  $\text{H}_3\text{PO}_4$  was different from that in  $\text{H}_2\text{SO}_4$ , despite that the path of bubble streamer were very similar. In single-bubble, the SL intensity in 30 wt%  $\text{H}_3\text{PO}_4$ , where the SBSL could reach the maximum due to the viscosity by simulation, was almost the same as that in water. The results suggest that a key factor may exist for bright SL other than vapor pressure and viscosity.

#### Acknowledgment

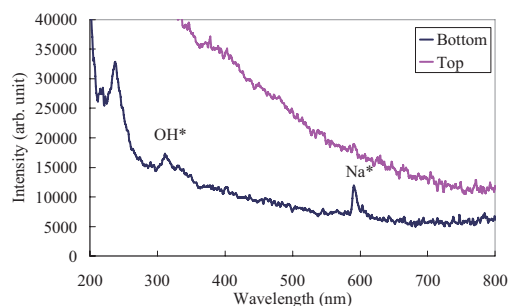
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#### References

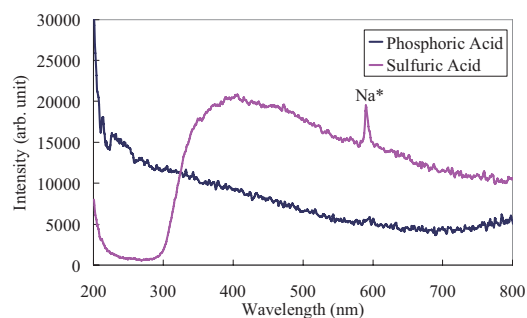
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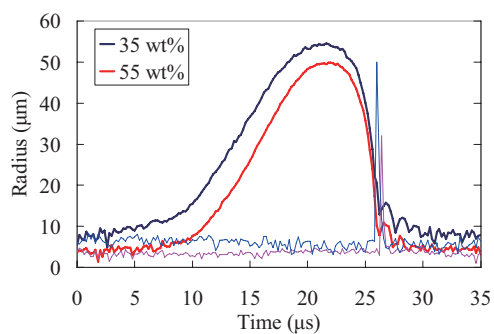
**Fig. 3.** MBSL photos in 1 M  $\text{Na}_3\text{PO}_4$ - $\text{H}_3\text{PO}_4$  solution for (a) 10, (b) 20, and (c) 30  $\text{W}/\text{cm}^2$ , and in 1 M  $\text{Na}_2\text{SO}_4$ - $\text{H}_2\text{SO}_4$  solution for (d) 10, (e) 20, and (f) 30  $\text{W}/\text{cm}^2$  in ultrasonic intensity.



**Fig. 4.** Corresponding MBSL spectra to the photo for  $\text{H}_3\text{PO}_4$  shown in Fig.2(b) in the bottom region and the top region (near the horn tip).



**Fig. 5.** Comparison of MBSL spectra between 1 M  $\text{Na}_3\text{PO}_4$ - $\text{H}_3\text{PO}_4$  and 1 M  $\text{Na}_2\text{SO}_4$ - $\text{H}_2\text{SO}_4$  in an ultrasonic cleaning bath at 32 kHz.



**Fig. 6.** Radius-time curve of a sonoluminescing single-bubble in 35 and 55 wt%  $\text{H}_3\text{PO}_4$  (aq.).