

Sonochemical degradation of phenol and aniline in aqueous solution

フェノールとアニリンの2成分を含む水溶液中での
超音波分解

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1. Introduction

When high intensity ultrasound is irradiated to solution, micro bubbles, which are called cavitation bubbles, generate with high temperature and high pressure. It is reported that the sonochemical reaction happens at the inside of cavitation bubbles and their interface.

Here, the regions where the sonochemical reaction takes place is separated into three parts. One is "Inside of bubble", the second is "Gas/liquid interface", and the third is "Interfacial region" (Fig. 1). "Inside of bubble" is high pressure and high temperature so OH radicals are generated by pyrolysis of water in this region. Direct pyrolysis reactions of organic solutes also occur. "Gas/liquid interface" is the region where the solutes are pyrolyzed and react with OH radicals that has diffused from the inside of cavitation bubbles. "Interfacial region" is spatial region and the solutes in this region are degraded by the heat diffused from cavitation bubbles and reaction with OH radicals.

In this study, ultrasound was irradiated to aqueous solution containing types of organic solutes. The solutes used in this study are phenol, sodium octyl benzene sulphonate (OBS) and aniline. Interaction of different solutes or the reaction region of each solute were discussed on the basis of the amounts of sonochemical degradation.

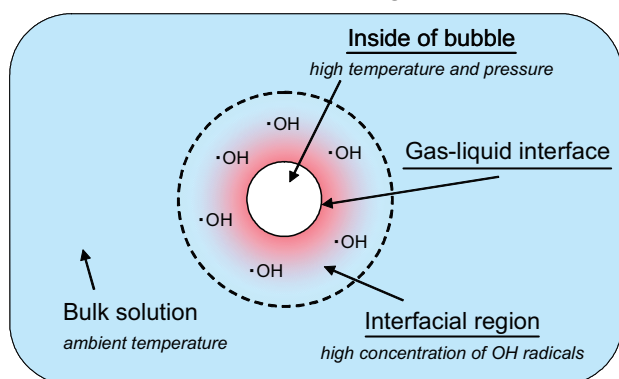


Fig. 1 Three reaction regions where sonochemical reactions take place.

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2. Experimental

Ultrasound irradiation was carried out using a 65 mmφ oscillator (Kaijo 4611type; MFG. No.91F2) and an ultrasound generator (Kaijo TA-4021type; Lot. No.19G9, frequency; 200 kHz), which was operated at 200 W. A 60 mL Ar-saturated aqueous solution containing phenol and aniline or OBS was sonicated in a water bath, which was maintained at 20°C by a cold water circulation system. When the competing reactions of phenol/aniline and phenol/OBS were carried out, the total concentration of solute was kept at 100 μM, 200 μM, 300 μM. Then, the concentration ratios of phenol/aniline and phenol/OBS were kept at 0/6, 1/5, 2/4, 3/3, 4/2, 5/1, 6/0, respectively.

Hydrogen peroxide yields were measured by the KI method using a spectrophotometer. The concentration of phenol, aniline and OBS were monitored by a high-performance liquid chromatograph (HPLC) with UV detection at 222 nm using a ODS column with a mobile phase of acetonitrile/water (20:80 v/v ; phenol/aniline, 50:50 v/v ; phenol/OBS) flowing at 0.3 mL min⁻¹. Surface tension was measured at ca. 20°C using a laboratory-made surface tension meter employing the Wilhelmy plate, attached to an electronic balance via a thin metal wire.

3. Results and Discussion

As a result of surface tension measurement for the solutes used in this study, the surface tension of OBS decreased as the concentration of solution increased. On the other hand, in the cases of phenol and aniline (less than 500 μM), there were practically no change in the surface tension of each solute compared with that of water. Moreover, it is reported that phenol has relatively higher hydrophobicity than aniline and the rate of degradation is affected by the degree of the hydrophobicity. Based on the report[1], it was suggested that the easiness of solute accumulation to the bubble interface is OBS > phenol > aniline.

Ultrasound was irradiated to aqueous solution containing phenol and OBS (total concentration ; 100 μM). This result was shown in Fig. 2. It can be seen that there was curve relation

between the initial concentration and degradation. When a small amount of OBS and a large amount of phenol were contained in aqueous solution, the degradation of phenol was critically inhibited. On the other hand, when a large amount of phenol and a small amount of OBS were contained in aqueous solution, the degradation of OBS was not so inhibited. Thus the easiness of solute accumulation to the bubble interface was $OBS > phenol$. This result corresponded with the result of the surface tension measurement. Similar results were also obtained in the other total concentration (total concentration ; 200, 300 μM). From these results, it was considered that the reaction region of phenol and OBS was different. In our opinion, the main reaction region of OBS was suggested to be "Gas/liquid interface" and the main reaction region of phenol was "Interfacial region".

Secondly, ultrasound was irradiated to aqueous solution containing phenol and aniline (total concentration ; 100 μM). This result was shown in Fig. 3. It can be seen that there was linear relation between the initial concentration and degradation. Thus the degradation ratio was suggested to be constant between phenol and aniline. From Fig. 3, the degradation ratio of phenol could be calculated to be 1.6 times larger than that of aniline. Moreover, similar results were obtained in the other total concentration (total concentration ; 200, 300 μM). From these results, it was considered that the main reaction region of phenol and aniline was almost the same and the main reaction region of phenol and aniline was suggested to be "Interfacial region".

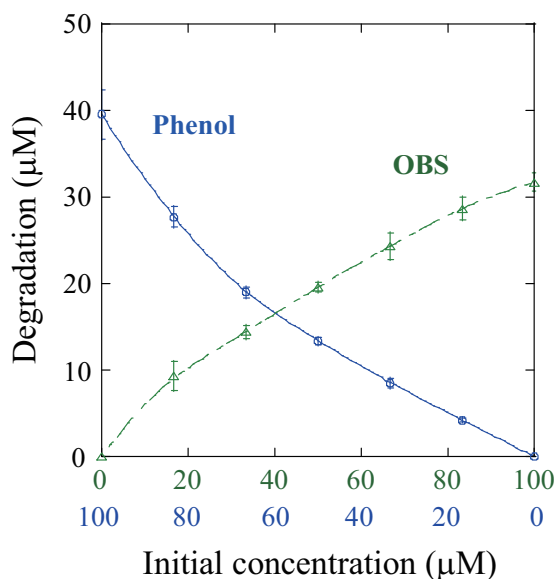


Fig. 2 Changes in concentration of phenol and OBS in phenol/OBS aqueous solutions. (Total concentration of phenol and OBS ; 100 μM Irradiation time ; 10 min)

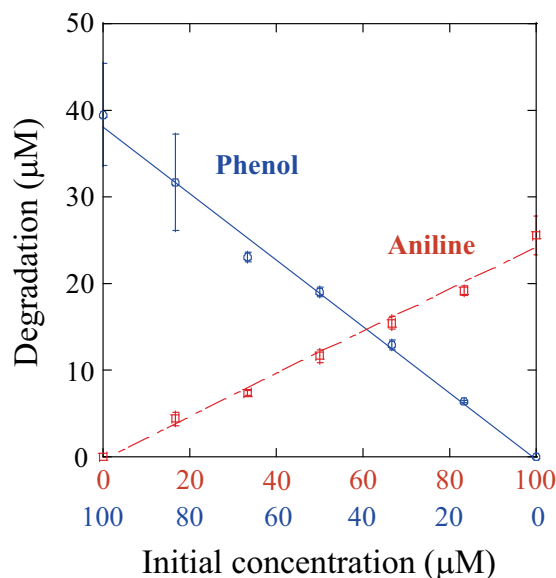


Fig. 3 Changes in concentration of phenol and aniline in phenol/aniline aqueous solutions. (Total concentration of phenol and aniline ; 100 μM Irradiation time ; 10 min)

4. Conclusions

In the case of the competing reactions of phenol and aniline, there was linear relation between the initial concentration and degradation. On the other hand, in the case of the competing reactions of phenol and OBS, OBS was more easily accumulated at "Gas/liquid interface" than phenol. It was also suggested that the main reaction region of phenol and aniline was "Interfacial region" and the main reaction region of OBS was "Gas/liquid interface".

5. References

- [1] B. Nanzai, K.Okitsu, N. Takenaka, H. Bandow and Y. Maeda : *Ultrason. Sonochem.* **15** (2008) 478.