

## Size-Dependent Belousov–Zhabotinsky Oscillation in Small Beads

Kenichi Yoshikawa,<sup>\*,†</sup> Ryoichi Aihara,<sup>‡</sup> and Konstantin Agladze<sup>§</sup>

Department of Physics, Faculty of Science, Kyoto University, Kyoto 606-8502, Japan; Bio-Mimetic Control Research Center, The Institute of Physical and Chemical Research (Riken), Nagoya 463-0003, Japan; and Institute of Theoretical and Experimental Biophysics, Pushchino, Moscow Region, 142292, Russia

Received: May 5, 1998; In Final Form: June 23, 1998

We examined chemical oscillations in the Belousov–Zhabotinsky (BZ) reaction with spherical ion-exchange resin beads (radius: 0.1–0.4 mm) loaded with a cationic catalyst, ferroin, in which no traveling wave appears and the oscillation is synchronized over individual beads. The period of the oscillation increases with a decrease in the size of the beads. Based on a theoretical consideration of the effect of the diffusion of active species through the surface of the bead reactor into the bulk aqueous solution, the following relationship was deduced:  $f/[\text{H}_2\text{SO}_4]^\gamma \propto (1 - \eta/R)$  where  $f$  is the frequency (Hz) of the oscillation,  $R$  is the radius (mm) of the beads,  $[\text{H}_2\text{SO}_4]$  is the concentration (mol/dm<sup>3</sup>) of sulfuric acid, and  $\gamma$  and  $\eta$  are constants. This relationship was consistent with experimental results with values of  $\gamma = 1.4$  and  $\eta = 7.4 \times 10^{-4}$ .

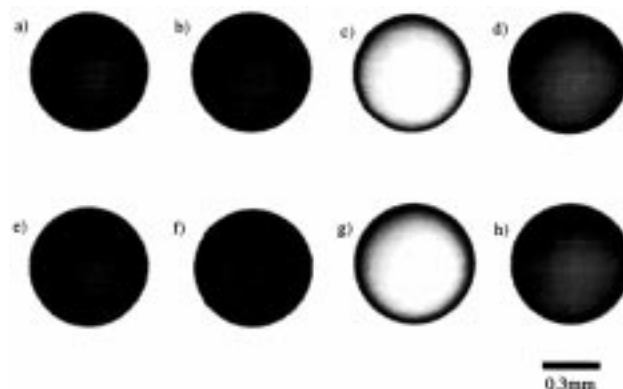
## Introduction

Temporal oscillations and propagating waves in excitable media are well-known reflections of spatiotemporal self-organization in dissipative systems.<sup>1</sup> Generally, such phenomena can be described by so-called reaction–diffusion equations under the framework that the medium is uniform and homogeneous.<sup>2–4</sup> Thus, symmetry breaking in the spatiotemporal structures often arises in the absence of any spatial inhomogeneity, regardless of the boundary conditions. On the other hand, there are several excitable systems in the real world that are not continuous in space: e.g., in excitable biological tissues, excitation propagates in cells separated from one another, and in heterogeneous catalytic reactions, active catalyst grains are separated by the reaction medium. The separating medium is passive; in other words, it does not maintain the excitation dynamics. However, the medium can provide a diffusional link, or cross-talk, between separated elements.

One of the most popular models for studying chemical waves is the Belousov–Zhabotinsky (BZ) reaction.<sup>2–4</sup> In studies of the effect of heterogeneity, various media have been investigated using a catalyst-binding matrix, such as silica gel, ion-exchange resin, polysulfon membranes, and mesoporous glass.<sup>5–12</sup> The oscillatory reaction proceeds only where the catalyst is spatially available. A catalyst-free medium provides for the diffusion of the species generated in the catalyst-doped matrix. In the present study, we examined the behavior of an isolated single active element. We describe how the oscillating frequency depends on the size of catalyst-doped beads.

## Experimental Section

The experimental system was similar to that reported by Maselko et al.<sup>12</sup> 1,10-Phenanthroline and iron(II) sulfate heptahydrate (Wako Pure Chemical Industries, Ltd.) were used to prepare the ferroin solution. Sulfuric acid and malonic acid



**Figure 1.** Oscillating single bead (0.69 mm in diameter). The time interval between plates is 21 s. The entire bead changes instantaneously within the resolution of the video (1/30 s); i.e., no chemical wave is generated.

were obtained from Wako Pure Chemical Industries, Ltd., and potassium bromate was from Nacalai Tesque. These reagents were used without further purification. The cation-exchange resin (Dowex 50W-X4) was loaded with a ferroin solution of  $[\text{Fe}(\text{phen})_3^{2+}] = 3.6 \times 10^{-4}$  M, by mixing 1 g of beads with 10 mL of ferroin solution and then stirring gently for 1 h. These beads were dried for 240 h at room temperature and then arranged on the bottom of the reaction solution. All measurements were carried out at  $23 \pm 1$  °C. All observations were made on a Petri dish (5 cm in a diameter) under a microscope and were recorded on videotape using a CCD camera (CCD-S1, Shimadzu). A time trace of the light intensity of the beads was obtained using an image processor (Himawari, Library Co. Ltd.). In each video frame, a  $1 \times 1$  pixel corresponds to  $3.8 \times 3.8 \mu\text{m}$ . The oscillatory period is represented as the average of 10 consecutive oscillations.

## Results

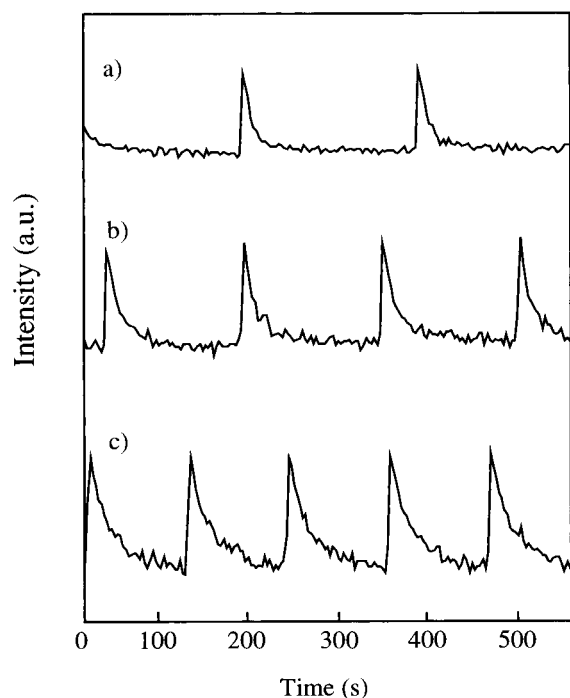
Figure 1 shows the oscillation of an isolated ion-exchange resin bead in a BZ solution of  $[\text{CH}_2(\text{COOH})_2] = 0.4$  M,  $[\text{KBrO}_3] = 0.2$  M, and  $[\text{H}_2\text{SO}_4] = 1.0$  M. Beads loaded with catalyst

\* To whom correspondence should be addressed.

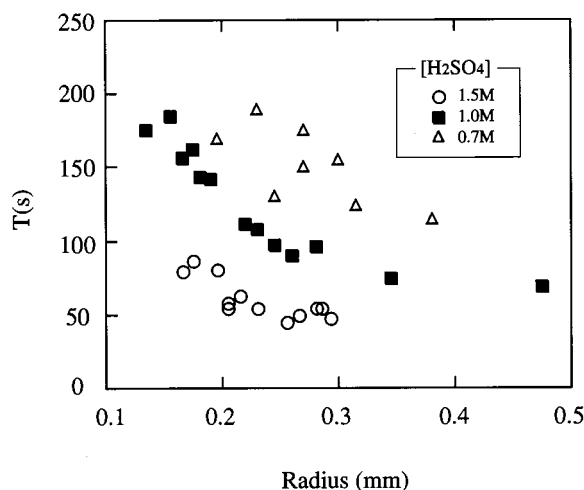
† Kyoto University.

‡ The Institute of Physical and Chemical Research.

§ Institute of Theoretical and Experimental Biophysics.



**Figure 2.** Time traces of the light intensity of catalyst-doped spherical beads of radii: (a) 0.30, (b) 0.44, and (c) 0.56 mm.  $[\text{H}_2\text{SO}_4] = 1.0 \text{ M}$ .



**Figure 3.** Dependence of the oscillatory period  $T$  on radius of bead;  $[\text{H}_2\text{SO}_4] = 1.5, 1.0, \text{ and } 0.7 \text{ M}$ .

were put into a Petri dish containing a 5 mm layer of BZ solution. The measurements were performed on individual single beads, situated far enough (more than 5 mm) from other beads. A periodic change in the color of the bead was clearly observed under a microscope and recorded on videotape. In accordance with previous studies by Maselko et al.,<sup>12</sup> sustained oscillations were generated with almost constant periodicity and amplitude for more than several hours with the ferriin-loaded catalyst.

Figure 2 shows oscillations represented as the gray level of the beads, where the high and low levels correspond to the oxidized and reduced states, respectively. Under our experimental conditions with a time resolution of 1/30 s, no traveling chemical wave was generated on individual beads; i.e., the entire bead changed color instantaneously.

Figure 3 shows the dependence of the period of oscillation on the size of the bead. The period decreased monotonically with an increase in bead size. For beads smaller than 0.2 mm,

no oscillations were observed. However, the system was excitable: it was possible to induce oscillation by touching beads with a silver wire. This suggests that the BZ reaction tends to be inactivated with a decrease in bead size. A natural assumption is that this effect in smaller beads is related to dissipation of the activator through the surface of the bead. Thus, this size-dependent oscillation phenomenon is similar to a classic radioactive critical mass phenomenon. Oscillations can start only if a critical active mass is exceeded so that the activator is produced faster than it is dissipated.

In a related study with a similar BZ system of silica gel with a fixed catalyst, it has been shown that there is a critical layer thickness for the waves to propagate.<sup>13</sup> A decrease in the thickness of the active layer enhances the role of diffusion of the autocatalytic species ( $\text{HBrO}_2$ ) into the inactive part of the medium.

### Theoretical Analysis and Discussion

Let us discuss the experimental findings based on the theoretical framework of the Oregonator. By reducing the three variables in the Oregonator to two variables with the elimination of the fast variable, the following equations are obtained:<sup>14</sup>

$$\epsilon \frac{dx}{d\tau} = x - x^2 - 2q\alpha \frac{z}{1 - zx + \mu} \quad (1)$$

$$\frac{dz}{d\tau} = x - \alpha \frac{z}{1 - z} \quad (2)$$

where  $x$  and  $z$  are the dimensionless concentrations of  $\text{HBrO}_2$ ,  $X$ , and ferriin,  $Z$ .  $X = (k_1A/2k_4)x$ ,  $Z = Cz$ ,  $A = [\text{BrO}_3^-]$ ,  $C = [\text{Fe}(\text{phen})_3^{2+}] + [\text{Fe}(\text{phen})_3^{3+}]$ ,  $\epsilon = k_1A/k_4C$ ,  $\alpha = k_4K_8B/k_1^2A^2h_0^2$ ,  $\mu = 2k_4k_7/k_1k_5$ ,  $t = (k_4C/k_1^2A^2h_0)\tau$ , and  $q$  is the stoichiometric factor. These equations are the modified version of the Oregonator, corrected for the interpretation of kinetics when ferriin is used as a catalyst. From the analysis of dynamics in eqs 1 and 2, by taking  $\epsilon \sim 10^{-2}$ , it has been previously indicated that the oscillatory period is mostly determined by the kinetics of the first-order term in eq 1:

$$\epsilon(dx/d\tau) \cong x \quad (3)$$

This means that the period  $T$  of the oscillation is proportional to  $\epsilon$ .

$$T \propto \epsilon \quad (4)$$

Next, we will discuss the effect of the diffusion of chemical species within the beads on the periodicity of the oscillation. In general, the time  $\tau_d$  needed for the diffusion over distance  $l$  is given by

$$\tau_d \sim l^2/D \quad (5)$$

Since  $D$  is on the order of  $10^{-5} \text{ cm}^2 \text{ s}^{-1}$  in a normal aqueous environment, the time required  $\tau_d$  for diffusion of 0.1 mm is  $\tau_d \sim 10 \text{ s}$ . In our experiment, the period of the oscillation was on the order of minutes. This means that, roughly speaking, bead oscillation is generated under conditions of a well-stirred reactor for individual beads a few submillimeters in diameter. In addition, with a bead diameter on the order of a few submillimeters, we can neglect spatial effects within the bead oscillator. This consideration is consistent with previous studies on the bead oscillator in the BZ reaction. Maselko and Showalter reported a clear spiral pattern using the beads with a radius of 0.7 mm.<sup>15</sup> On the other hand, Nishiyama observed temporal

oscillation in beads ranging from 35 to 75  $\mu\text{m}$  in radius and reported that no chemical wave was generated with such small beads.<sup>16</sup>

We now address the effect of bead size on periodicity. During the gradual increase in  $\text{HBrO}_2$  ( $x$  in eq 1) in the rate-determining step,  $\text{HBrO}_2$  would escape from the bead into the bulk aqueous solutions. Since there is no catalyst in the bulk solution, it is highly likely that there should be no production of  $\text{HBrO}_2$  outside the bead. Thus, the rate of the decrease in the concentration of  $\text{HBrO}_2$ ,  $x$ , in the beads is expected to be proportional to the ratio of  $S$  to  $V$  (volume) or to  $1/R$ , since the total number of  $\text{HBrO}_2$  molecules is proportional to  $V$ . Thus, the rate of the gradual increase in the rate-determining process (see eq 3) is given by

$$\begin{aligned} \epsilon \frac{dx}{d\tau} &\cong x - \frac{\eta}{R}x \\ &= \left(1 - \frac{\eta}{R}\right)x \end{aligned} \quad (6)$$

From this relationship it is clear that the period of oscillation given in eq 4 should be rewritten as

$$T \propto (1 - \eta/R)^{-1} \epsilon \quad (7)$$

Based on the mechanism included in the Oregonator, it is expected that  $\epsilon$  is expected roughly proportional to  $[\text{H}^+]^{-1}$

$$f/[\text{H}^+] \propto (1 - \eta/R) \quad (8)$$

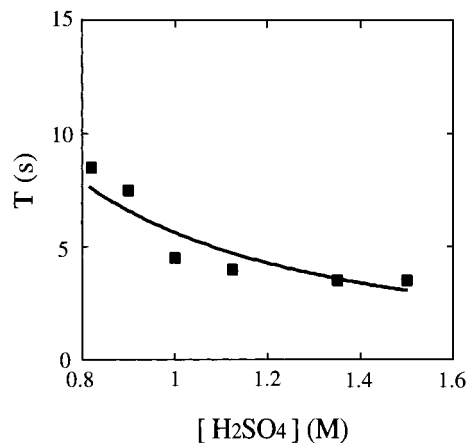
In applying eq 8 to our experimental results, we must consider that it is difficult to precisely measure the pH, or the activity of proton, in a highly acidic medium with a conventional pH electrode. In addition, it is natural to consider that the concentration of  $[\text{H}_2\text{SO}_4]$  is associated with the network of elementary reactions in the BZ reaction in a rather complicated manner. Thus, we would like to replace  $[\text{H}^+]$  by  $[\text{H}_2\text{SO}_4]^\gamma$  as in eq 9, where  $\gamma$  is close to unity. Thus, the frequency may be better interpreted with

$$f/[\text{H}_2\text{SO}_4]^\gamma \propto (1 - \eta/R) \quad (9)$$

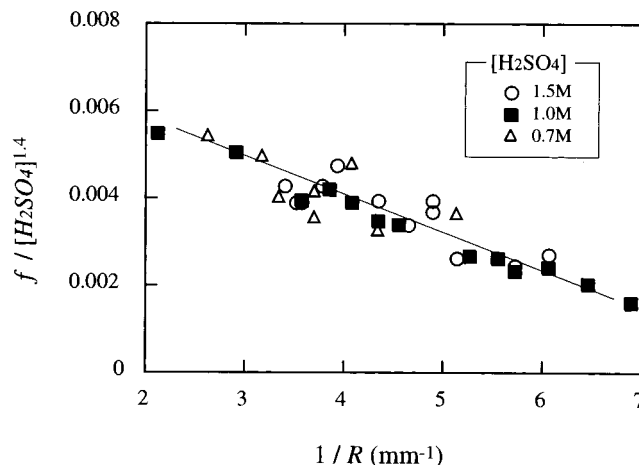
The dibasicity of sulfuric acid does not affect the proportionality in eq 9. In a study of manganese-catalyzed oscillations, Rastogi et al. reported that  $\gamma = 1.0$ .<sup>17</sup> On the other hand, Smoes reported that  $\gamma = 2.7$  in ferriin-catalyzed oscillations and noted that the periodicity and the mechanism of the oscillations are highly dependent on the ferriin concentration.<sup>18</sup> Thus, we examined, by ourselves, the  $[\text{H}_2\text{SO}_4]$  dependence of the frequency of the oscillation in a batch reactor with the similar concentrations of the reactants in the experiments on the beads oscillation;  $[\text{CH}_2(\text{COOH})_2] = 0.4 \text{ M}$ ,  $[\text{KBrO}_3] = 0.2 \text{ M}$ , and  $[\text{Fe}(\text{phen})_3^{2+}] = 0.9 \times 10^{-4} \text{ M}$ . Figure 4 indicates we found that  $\gamma = 1.7$  gives the best fit in this system.

In the bead oscillations, as shown in Figure 5, we found that  $\gamma = 1.4$  and  $\eta = 7.4 \times 10^{-4} \text{ mm}$  are most consistent with the experimental findings. The small difference in  $\gamma$  between the bulk and bead oscillations may be attributed to the change in the catalyst condition and also to a kind of stoichiometric effect.<sup>19</sup>

In conclusion, it has become clear that the reduction in the frequency of oscillation with smaller beads is associated with diffusion of the autocatalytic species from the surface of the beads into the bulk solution.



**Figure 4.**  $[\text{H}_2\text{SO}_4]$  dependence of the period  $T$  of the oscillation in a batch reactor (8 mL) under constant stirring with the reactions;  $[\text{CH}_2(\text{COOH})_2] = 0.4 \text{ M}$ ,  $[\text{KBrO}_3] = 0.2 \text{ M}$ , and  $[\text{Fe}(\text{phen})_3^{2+}] = 0.9 \times 10^{-4} \text{ M}$ .  $[\text{H}_2\text{SO}_4]$  dependence on the frequency is given as  $f \propto [\text{H}_2\text{SO}_4]^{1.7}$ .



**Figure 5.** Relationship between  $f/[\text{H}_2\text{SO}_4]^{1.4}$  and  $1/R$ , where  $f$  is the frequency in Hz and  $R$  is the radius of the bead in mm. The correlation coefficient of the linear relationship is 0.915 when  $\gamma = 1.4$  as in this figure, whereas correlation coefficients are 0.907 and 0.912 at  $\gamma = 1.3$  and  $\gamma = 1.5$ , respectively.

**Acknowledgment.** We are grateful for the fruitful discussion with Prof. A. M. Zhabotinsky. We thank the reviewer for helpful advice.

## References and Notes

- (1) Nicolis, G.; Prigogine, I. *Self-Organization in Nonequilibrium Systems*; Wiley: New York, 1977.
- (2) Zaikin, A. N.; Zhabotinsky, A. M. *Nature* **1970**, *225*, 535.
- (3) Winfree, A. T. *Science* **1972**, *175*, 634.
- (4) Murray, J. D. *Mathematical Biology*; Springer: Berlin, 1989.
- (5) Kuhnert, L. *Naturwissenschaften* **1983**, *70*, 464.
- (6) Agladze, K. I.; Krinsky, V. I.; Panfilov, A. V.; Linde, H.; Kuhnert, L. *Physica D* **1989**, *39*, 38.
- (7) Yamaguchi, T.; Kuhnert, L.; Nagy-Ungvarai, Zs.; Müller, S. C.; Hess, B. *J. Phys. Chem.* **1991**, *95*, 5831.
- (8) Maseko, J.; Showalter, K. *Physica D* **1991**, *49*, 21.
- (9) Munuzuri, A. P.; Innocenti, C.; Flessels, J. M.; Gilli, G. M.; Agladze, K. I.; Krinsky, V. *Phys. Rev. E* **1994**, *50*, 667.
- (10) Agladze, K.; Aliev, R. R.; Yamaguchi, T.; Yoshikawa. *J. Phys. Chem.* **1996**, *100*, 13895.
- (11) Agladze, K.; Keener, J. P.; Müller, S. C.; Panfilov, A. *Science* **1994**, *264*, 1746.
- (12) Maseko, J.; Reckley, J. S.; Showalter, K. *J. Phys. Chem.* **1989**, *93*, 2774.
- (13) Aliev, R. R.; Agladze, K. I. *Physica D* **1991**, *50*, 65.
- (14) Rovinsky, A. B.; Zhabotinsky, A. M. *J. Phys. Chem.* **1984**, *88*, 6081.

- (15) Maselko, J.; Showalter, K. *Nature* **1989**, 339, 609.
- (16) Nishiyama, N. *Physica D* **1995**, 80, 181.
- (17) Rastogi, R. P.; Yadava, K. D. S.; Prasad, K. *Indian J. Chem.* **1974**, 12, 974.
- (18) Smoes, M.-L. *J. Chem. Phys.* **1979**, 71, 4669.
- (19) One of the reviewers gave us a useful comment on the  $\gamma$  value, suggesting that the effective  $[\text{H}_2\text{SO}_4]$  should be evaluated by subtracting the concentration of  $\text{KBrO}_3$ , 0.2 M, because one proton of  $\text{H}_2\text{SO}_4$  as the

monoprotic acid in highly acid medium would be consumed to titrate  $\text{KBrO}_3$ . The authors agree with this comment and think that additional effects should also be considered, such as the change in the first and second dissociations in  $\text{H}_2\text{SO}_4$ , activities of the individual chemical species in addition to  $[\text{H}^+]$ , and the difference in the concentrations of "charged" species within and outside the beads as the ion-exchange matrix. In the present article, it may be appropriate for us to mention that the effect of the acidity on the BZ reaction has not been fully clarified yet and remains as one of the problems to be solved in the near future.