The Comparison of the Bead Size Effect on the Two Wave Patterns Induced in One Reaction System

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Received May 16, 2001

We have studied the characteristic wave propagation in 1,4-CHD-Bromate-Ferroin reaction system and we have examined the bead size effect on the wave propagation of the system by adopting a half-divided Petri dish which is separated into two parts by the size of cation-exchange resin. It has been done to understand the reaction process inducing the characteristic wave behavior in the system. The characteristic wave behavior of the system is in the spontaneous induction of a revival wave with a long time lag. We have obtained a result that the revival wave is not affected by the size of catalyst-doped beads while the initially induced wave is influenced by the size of beads. It means that the two waves are induced by different reaction processes each other and the revival wave is induced by an uncatalyzed reaction process.

Keywords : Bead size effect, 1,4-CHD system, Revival wave.

Introduction

Since Luther presented the concept of macroscopic waves and patterns developing from chemical reaction mixing with diffusion,[1] many studies on the chemical waves have been carried out on the homogeneous and inhomogeneous reaction mixtures.[2,3] The Belousov-Zhabotinsky (BZ) reaction is one of the most popular model for studying chemical waves.[4,5]

Physico-chemical systems of small size as well as biological tissues may also self-organize into coherent spatio-temporal activity. These biological systems include heart muscle, aggeregating cells in the slime mold Dictyostelium discoideum, calcium waves in xenopus oocytes, and spreading depression in chicken retina.[6-9] For the studies of the chemical wave propagation in the heterogeneous condition, various systems using a catalyst-binding matrix, such as silica gel, polysulfone membranes, and ion-exchange resin have been investigated.[10-17] The BZ reaction with ferroin-catalyst immobilized on beads of cation-exchange resin offers a convenient experimental system for studying an inhomogeneous excitable medium. Maselko *et al.* have studied regular and irregular spatial wave behaviors in the BZ reaction system with ferroin catalyst varying cation-exchange resin size and concentration of reaction solution.[16] Yashikawa *et al.* have reported how the oscillating frequency in a single particle depends on the bead size with similar experimental system of Maselko *et al.*[17]

This study focuses on the behaviors of the wave propagation in the modified BZ reaction system using 1,4-cyclohexanedione instead of malonic acid as an organic substrate with ferroin catalyst immobilized on cation-exchange resin. In the reaction system, a characteristic wave behavior in which a revival wave is induced spontaneously with a long time lag has been reported by Huh *et al.*, recently.[18] It is an unusual phenomenon that has not been obtained in the BZ reaction using malonic acid. By the experimental results of Huh *et al.*, the pattern of the revival wave is much different from that of the initially induced wave. In the BZ reaction using a similar reaction system, an initially induced wave propagates continuously without a break for a new wave. In order to understand the mechanism for the characteristic wave behavior obtained in the system in more detail, we have examined the bead size effect on the wave propagation of the system. The experiment has been carried out in a specially designed half-divided Petri dish which is able to be separated into two parts only by the bead size of cation-exchange resin. In the system, the reaction solution is in the same condition throughout the whole dish, but the dish is divided into two parts artificially by the bead size of cation-exchange resin. In the experiments using two separate dishes to examine the bead size effect on the wave propagation, the comparison of the bead size effect between two wave patterns induced with time lag in same dish is not able to be obtained. In the experiments using separate dishes, a simple comparison of the bead size effect for a certain wave pattern can be obtained as shown in the studies by Maselko *et al*.[16]

The diketonic compound such as 1,4-CHD is well known being suitable for the gas-free BZ reactions,[19,20] however, the reaction mechanism in a BZ-type reaction using 1,4-CHD compound instead of malonic acid has not been understood well since the reaction intermediates are very complex in the 1,4-CHD reaction system. Thus, anomalous behaviors that have not been known in the BZ reaction have been obtained in the system. For example, Manz *et al*. have studied an anomalous dispersion of chemical waves in a homogeneous catalyzed reaction of the 1,4-CHD system recently.[21]

Experimental Section

The working solutions were prepared from stock solutions of $NaBrO_3$, 1,4-CHD, $Fe(phen)_3SO_4$, and sulfuric acid. All reagents were used in their commercial grade without further purification. Two different mesh ranges of analytical grade cation-exchange resin (Sigma, Dowex 50W-X4) with mesh 400 (bead diameter 40-70 mm) and mesh 200 (bead diameter 70-150 mm) were used. The cation-exchange resin was washed several times for acidity with distilled water and dried at filter paper. Then the resin was loaded with ferroin by mixing a measured quantity of resin beads with a measured volume of ferroin solution and stirring gently for 1 hour.

The reaction vessel which is consisted of a covered Petri dish of 10 cm in diameter was manufactured by a special order. The dish is separated into two parts by a thin glass plate before the reaction suspension solution is poured into the dish. The dividing plate was manufactured by considering the size of used Petri dish, and a thin glass plate of 0.5 mm in thickness was used for it. Two suspensions containing same reaction solution and different bead size of ferroin-doped resin were prepared in two beakers separately. The total volume of the two suspensions are the same each other. The two suspensions are poured simultaneously into each part of the divided dish and settled on the dish some period. When the suspension solution containing ferroin-doped resin forms a uniform thin film in both parts of the dish, the dividing thin glass plate was removed carefully from the dish to allow the mix of reaction solution throughout the whole dish. A thin groove was made on the side wall of the dish to help fixing and removing of the dividing glass plate. Then, a boundary was continued by a difference of the bead size of cation-exchange resin although the thin glass plate was removed.

The experiments were monitored with a digital imaging system. An image from a CCD camera (Sony, SSC-370) attached to a zoom lens (Niko, 1.4X) was processed into image analyzing program (Flash Point, Optimus 6.1). The overall scheme of an experimental apparatus for the experiments is well described in Figure 1.

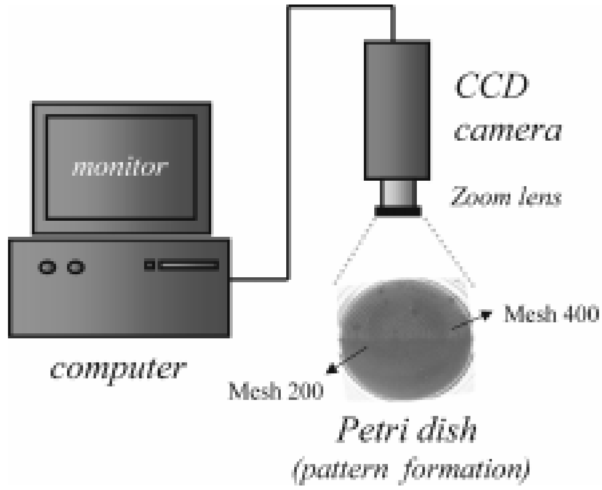


Figure 1. The overall scheme of the experimental apparatus for the half-divided Petri dish system.

Results and Discussion

The Characteristic Wave Behaviors in 1,4-CHD-Bromate-Ferroin Reaction System. At first, We have carried out an experiment in a non-divided dish using the reaction system before we have studied the bead size effect on the system in a half-divided dish. The Petri dish for the experiment was filled with the bead size of mesh 400 resin.

The resin formed a thin uniform film on the bottom of the reaction Petri dish after the reaction mixture was settled on the dish. The initial color of the thin film was green by the oxidized catalyst ion. After an induction period about 60 min being dependent on the concentration of the initial reactant, reddish spots have been formed spontaneously on the resin film. A spiral wave was initiated from each spot with a high frequency. These behaviors for the wave initiation are similar with the results obtained in the BZ reaction using malonic acid in a similar same experimental condition.[16]

However, a large difference has been obtained from the BZ system as reaction time goes on for a long period. A break of the wave propagation has been obtained in the system using 1,4-CHD compound, while no break has been obtained in the BZ reaction in a similar reaction condition. Figure 2 shows a typical pattern of the wave propagation in

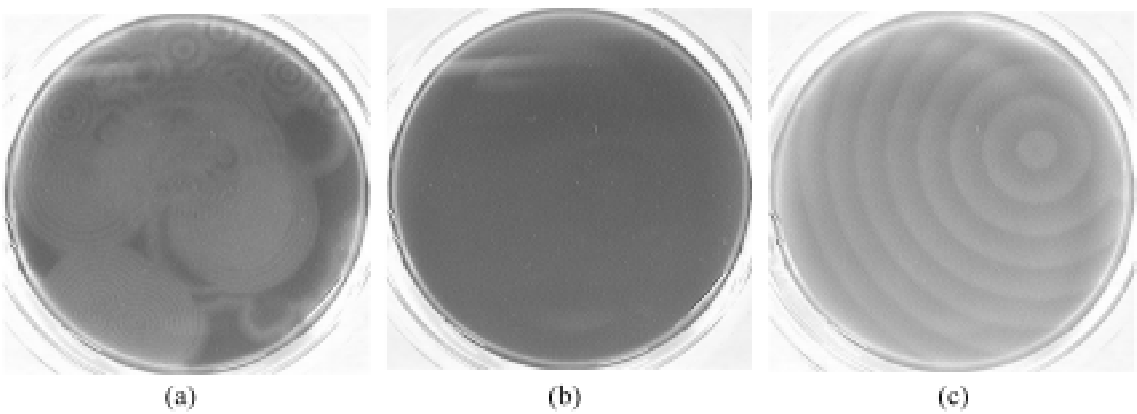


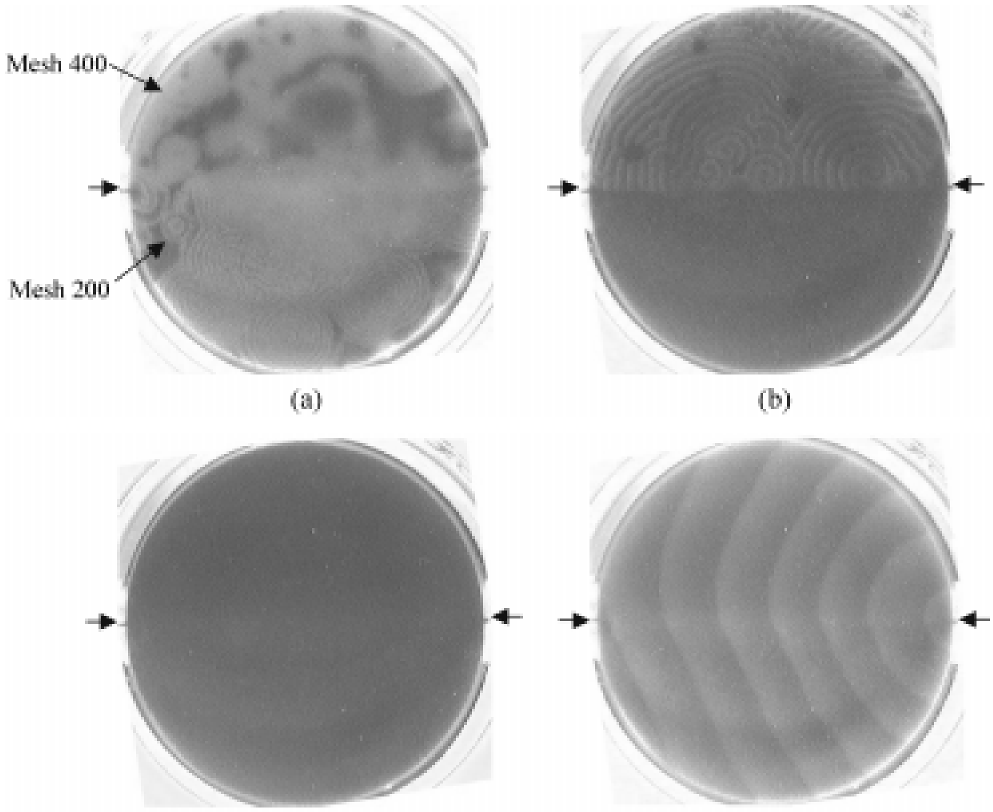
Figure 2. Typical pattern of the wave propagation obtained from the reaction system of 1,4-CHD-Bromate-Ferroin in a non-divided Petri dish filled with the resin of mesh 400. The initial reaction condition corresponds to $[1,4\text{-CHD}]_o = 0.05$ M, $[BrO_3^-]_o = 0.15$ M, $[\text{ferroin}]_o = 1.5 \times 10^{-3}$ M, and $[H^+]_o = 1.0$ M. The time of reaction process is 80 min in (a), 300 min in (b), and 1300 in (c) after pouring into the Petri dish.

the 1,4-CHD system. Figure 2a shows the propagating wave at the initial period of the 1,4-CHD system. The initially induced wave shows an irregular spiral pattern with a high wave frequency and is not much different from the propagating wave obtained in the BZ reaction using malonic acid.[16] However, a characteristic wave behavior is obtained in the 1,4-CHD system as reaction time goes on for a long period. A break of the wave propagation has been obtained in the 1,4-CHD system as shown in Figure 2b and no wave has been obtained during that period. And a new wave has been induced spontaneously after the period. The pattern of the new wave which is a revival wave in the system is much different from the pattern of the initially induced wave as shown in Figure 2c. It is a concentric target pattern with longer wavelength. However, in the BZ reaction system the propagation of the initially induced wave continues without a break period. A detailed wave behavior for the 1,4-CHD system in a non-divided Petri dish has been well explained by Huh *et al*.[18]

The Wave Propagation of the 1,4-CHD System in a Half-Divided Petri Dish. As shown in Figure 2, two consecutive waves have been obtained in the 1,4-CHD system. The two patterns have different characters in many wave behaviors. Thus, in this study we have compared the characters of the two waves by the bead size effect of cation-exchange resin on the wave propagation.

Figure 3 shows a typical pattern of the wave propagation of the system in a half-divided Petri dish. The behaviors of the initial wave shown in Figure 3a and in a half part of Figure 3b were much influenced by bead size difference. The induction time for the wave initiation was always shorter in the part with larger beads of resin. An easy ignition of chemical wave in the part with larger beads of resin is able to be explained by the fact that high surface curvature of the small beads results in these beads being more difficult to excite. This result is consistent to the experiment result using two separate dishes in the BZ reaction.[16] By measuring the position as function of time in the computer image, the wavelength was a little shorter and the wave velocity was some higher in the part with larger beads of resin.

In addition, the duration period of the initially induced wave was shorter in the part with larger beads of resin as shown in Figure 3b. In our experimental system using a half-divided Petri dish, the difference of the duration period of the initial wave has been obtained vividly. If we use separate dishes for the bead size effect, a small difference of the duration period is not able to be detected clearly because of other experimental factors. The short duration period in the part with larger beads of resin is able to be explained by the fact that the rapid activation of the large beads brings out the change of the reaction system more rapidly. In the break period after the initially induced wave has disappeared in both parts of the dish, the whole dish has same color without separating boundary and no wave has been formed in the



(a) (b) (c) (d)

Figure 3. The behavior of the wave propagation of the reaction system when it was carried out in a half-divided Petri dish with the same initial condition used for Figure 2. The time of reaction process is 90 min in (a), 180 min in (b), 220 min in (c), and 1200 min in (d).

Table 1. The summary on the behavior of the wave propagation in 1,4-CHD-Bromate-Ferroin reaction system in a half-divided Petri dish

	Initial wave		Break period		Revival wave	
	mesh 200	mesh 400	mesh 200	mesh 400	mesh 200	mesh 400
Wave pattern	mixed spiral	spiral	no wave	no wave	concentric target	concentric target
Induction time (min)	60-70	80-90	150-180[a]	180-230[a]	1000-1200[b]	1000-1200[b]
Wavelength (mm)	0.5-1.0	1.0-2.0	no wave	no wave	10-20	10-20
Wave velocity (mm/min)	1.4-1.6	1.5-2.0	no wave	no wave	0.5-0.8	0.5-0.8
Duration period (min)	100-150	130-200	1000-1200	1000-1200	1200-2400	1200-2400

[a] It means the sum of the induction time and duration period of the initial wave. [b]It corresponds to the break period.

dish as shown in Figure 3c.

However, the effect of the bead size on the wave propagation was insignificant in the revival wave of the reaction system as shown in Figure 3d. The wave was initiated at a spot site and the wave propagated as a concentric target pattern regardless of the bead size difference. This result means that the revival wave induced spontaneously with a long time lag is not influenced much by the bead size of catalyst-doped resin. The propagation of the revival wave in a half-divided dish shown in Figure 3d is not much different from the propagating wave in a non-divided dish shown in Figure 2c. In summary, the initially induced wave has a spiral pattern and it is influenced by the bead size difference of catalyst-doped resin, while the revival wave is a concentric target pattern with longer wavelength and it is not much influenced by the bead size difference of the used resin. The bead size effect on the behaviors of the propagating wave of the 1,4-CHD system in a half-divided dish is summarized in Table 1.

The Comparison of the Bead Size Effect on Two Wave Patterns Obtained in the 1,4-CHD Reaction System. In many cases, the BZ reactions have been explained on the basis of Field-Körös-Noyes (FKN) mechanism.[22] When we consider the fact that the reaction system of this study is only different from the BZ reaction in the used organic substrate, the characteristic wave behavior obtained in the 1,4-CHD system should be explained by the reaction mechanism in which the used organic compound is involved. The experimental result that two wave patterns are induced spontaneously in the consecutive reaction process offers a clue for solving the reaction mechanism for the system. By the FKN mechanism, the organic compound used in the BZ reaction has an important role in the Br^- regeneration process as a reductant. In the modified BZ reaction using 1,4-CHD and bromate, various organic compounds including 1,4-dihydroxybenzene (H_2Q), mono-bromohyderoquinone (BrH_2Q), 1,4-benzoquinone (Q), and mono-bromocyclohexanedione (BrCHD) are able to be produced as organic intermediates. By considering the reaction intermediates, some reaction mechanisms for the regeneration of Br^- are possible in the system. Thus, Huh *et al.* have suggested two separate Br^- regeneration processes for the two wave patterns of the system. By the suggestion, the two processes are distinguished by the role of ferroin catalyst in the oxidation reaction of organic compound for the regeneration of Br^-. They have suggested that the initial wave is induced by a catalyzed oxidation of BrCHD by ferroin catalyst for the regeneration process of Br^-, while the revival wave is induced by an uncatalyzed oxidation of H_2Q which is produced as a reaction intermediate. A detailed reaction process for the 1,4-CHD system inducing the two waves consecutively has been well explained by Huh *et al*.[18]

The experimental result obtained in this study by adopting a half-divided dish also supports the suggestion of the separate oxidation processes for the two wave patterns, *i.e.*, a catalyzed oxidation process for the initial wave and an uncatalyzed oxidation process for the revival wave. According to the experimental results by Yoshikawa *et al.*,[17] the traveling wave induced by the catalyzed oscillatory BZ reaction should be affected by the bead size of diffusion medium since the inhomogeneous BZ reaction tends to be inactivated with a decrease in bead size and therefore the oscillating frequency increase with increasing the size of catalyst-doped beads. An increased oscillating frequency in a single particle will bring out a little shorter wavelength in the propagating wave. By the experimental results of this study on the bead size effect, only the behaviors of the initial wave agrees with the result being studied by Yoshikawa et al for the bead size effect on the wave propagation in separate dishes. The result that the revival wave is not much affected by the size difference of catalyst-doped beads as shown in Figure 3d means that the revival wave should be organized by a reaction mechanism in which the catalyst has not an important role in the Br^- regeneration process. When we consider the reaction system used in this study, a possible reaction mechanism for the uncatalyzed oxidation process is the oxidation of H_2Q. The mechanism for the uncatalyzed oxidation of H_2Q in the 1,4-CHD system has been suggested by I. Szalai *et al*. first in the studies of the temporal oscillation of 1,4-CHD-Bromate-Acid reaction.[23]

Conclusions

We have studied the characteristic wave propagation of 1,4-CHD-Bromate-Ferroin reaction system and we have examined the bead size effect on the wave behavior of the system in a half-divided Petri dish. It has been done to understand the reaction process inducing the characteristic wave behavior. The characteristic wave behavior of the system is in the spontaneous induction of a revival wave with a long time lag. We have obtained a result that the revival wave is not affected by the size of catalyst-doped beads while the initially induced wave is affected by the bead size difference. It means that the two wave patterns of the system are induced by different reaction processes each other and the revival wave is induced by an uncatalyzed reaction process.

Acknowledgment. This work was supported by a grant No. 2000-1-12100-010-2 from the Korea Science and Engineering Foundation, and BK21 project of Korean Ministry of Education.

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