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Some Dynamical Features of a Bubble-Free Belousov-Zhabotinsky Reaction

Jiraporn Luengviriya [1], Chaiya Luengviriya [2, 3 +], Malee Sutthiopad [2, 3], Boosayarat Tomapatanaget [4], and Stefan C. Müller [5]

[1] Department of Industrial Physics and Medical Instrumentation, King Mongkut´s University of Technology North Bangkok, 1518 Pibulsongkram Road, Bangkok 10800, Thailand

[2] Department of Physics, Kasetsart University, 50 Phaholyothin Road, Jatujak, Bangkok 10900, Thailand

[3] Center for Advanced Studies of Industrial Technology, Kasetsart University, 50 Phaholyothin Road, Jatujak, Bangkok 10900, Thailand

[4] Department of Chemistry, Chulalongkorn University, Bangkok 10330, Thailand

[5] Institute of Experimental Physics, Otto-von-Guericke-University Magdeburg, Universitätsplatz 2, D-39106 Magdeburg, Germany

Abstract. An investigation on the influence of initial concentration of H_2SO_4 on the dynamics of a bubble-free Belousov-Zhabotinsky (BZ) reaction both in well-stirred and unstirred solutions is presented. This reaction has an advantage over the classical BZ reaction, as any disturbance of the system by CO_2 bubbles is avoided. For $[H_2SO_4] \geq 250$ mM, well-stirred solutions are self-oscillating between reduced and oxidized states. The oscillation period is found to decrease, while $[H_2SO_4]$ is increased. For the unstirred case, propagating wave fronts (oxidized state) on a background (reduced state) occur in a thin layer of the solutions, when $[H_2SO_4] \geq 150$ mM. The wave period and the wavelength decrease as $[H_2SO_4]$ is increased. Differently, the wave velocity increases with $[H_2SO_4]$. At the same concentration of H_2SO_4, the wave period in the unstirred systems is always shorter than the oscillation period in the well-stirred solutions.

Keywords: Oscillation, Propagating wave, Pyrogallol, Excitable medium, Self-organization

1. Introduction

The dynamical features of self-organization systems have been documented in many nonlinear systems [1, 2]. Among these, oscillatory media naturally transform forth and back between two states, whereas excitable media – being characterized by a resting, an excited (activated), and a refractory state – support the phenomenon of travelling excitation waves. Among various self-organizing biological and chemical media [3-10], the Belousov-Zhabotinsky (BZ) reaction [11] is probably the most intensively investigated one due to its convenient preparation and experimental procedures. However, the classical BZ reaction, with malonic acid as organic substrate, produces CO_2 bubbles which disturb the propagation of waves and their observation [12, 13].

In this work, we present an investigation on a bubble-free BZ reaction, in which pyrogallol (1,2,3-trihydroxybenzene) is utilized as substrate [14-20]. We study the effect of the initial concentration of H_2SO_4

+ Corresponding author. Tel.: +66 2 9428028; fax: +66 2 9428029.
E-mail address: fscicyl@ku.ac.th.

on the dynamics of well-stirred solutions and on the properties of propagating waves in a thin layer of unstirred solution.

2. Methods

BZ solutions were prepared from $NaBrO_3$, H_2SO_4, pyrogallol and ferroin, all purchased from Merck. Stock solutions of $NaBrO_3$ (1 M) and pyrogallol (1 M) were freshly prepared by dissolving powder in deionized water (conductivity ~ 0.056 µS cm^{-1}), whereas stock solutions of H_2SO_4 (2.5 M) and ferroin (25 mM) were commercially available. Appropriate volumes of the stock solutions were mixed and diluted in deionized water to form BZ solutions with five sets of initial concentrations of reagents: [H_2SO_4] was varied between 100 mM and 300 mM, where [$NaBrO_3$] = 150 mM, [pyrogallol] = 15 mM, and [ferroin] = 0.5 mM in all cases (see Table 1).

We investigated the dynamics of the BZ reaction in two types of samples: a well-stirred solution and a thin layer medium. A well-stirred solution was realized by placing a beaker containing the BZ solution of 10 ml in volume and a magnetic bar on a magnetic stirrer. In each experiment of a thin layer medium, a 10-ml volume of the BZ solution was poured into a transparent flat reactor oriented vertically [21] with dimensions of 100 mm×100 mm×1.0 mm. A silver wire was immersed vertically into the solution to initiate propagating waves. Both kinds of samples were observed in a spectrophotometric setup, as shown in Fig. 1. The sample was placed between a white light source and a colour CCD camera (Super-HAD, Sony). Images of the sample were recorded every second with a resolution of 0.10 mm $pixel^{-1}$. The room temperature was kept at 24 ± 1°C.

During the experiments, the well-stirred solutions switched between reduced and oxidized states, corresponding to their colour, red and blue, respectively. In our analysis, the colour images were converted to 8-bit gray scale ones. To reduce noise, the gray level of an area of about 40 pixels × 50 pixels (about one fourth of the beaker projection) in the images of well-stirred solution was averaged and traced in the course of time, as shown in Fig. 2. This way, the oscillation period was estimated. For the thin layer media, the propagating wave fronts had a blue colour on a red background, as shown in Fig. 3. The wavelength was measured as the distance between two adjacent fronts. The period was the duration which it took a wave front to travel for a distance of one wavelength. The velocity of the wave front was calculated as the ratio between wavelength and period.

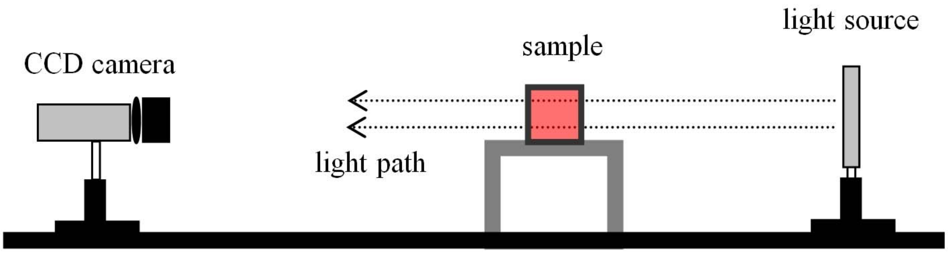

Fig. 1: Experimental setup. The sample is illuminated by a white light source and observed by a CCD camera. There are two types of samples: a well-stirred solution in a beaker and an unstirred medium in a vertical flat reactor.

3. Results and Discussion

Immediately after the BZ solution was prepared, it was in a reduced state and it had a red colour. For well-stirred solutions, we observed two types of long-term behaviour shown in Fig. 2. For a low concentration of H_2SO_4 ([H_2SO_4] ≤ 150 mM), the colour of the solutions was always red (low gray level), so they stayed in a reduced state. For [H_2SO_4] = 200 mM, a transient change from red to blue (low to high gray level) occurred once for a few minutes, and then the solution colour switched back to red and remained in this state. We observed oscillations in colour for [H_2SO_4] = 250 and 300 mM, that occurred after an induction time of 15 – 20 min. The oscillation period decreased, when [H_2SO_4] was increased: it was about 5.6 and 3.9 min for [H_2SO_4] = 250 and 300 mM, respectively.

Experiments on a thin layer of BZ solutions were performed with the same sets of initial concentrations. Wave initiation using a silver wire was not successful in the case of [H_2SO_4] = 100 mM. The medium remained red all the time, as in the experiments with the well-stirred solutions. However, propagating waves could be triggered in the unstirred medium for $[H_2SO_4] \geq 150$ mM. For these concentrations, the waves occurred in the unstirred system, whereas the well-stirred solutions either stayed in a reduced state (150 and 200 mM) or oscillated (250 and 300 mM).

The properties of the propagating waves depended on the concentration of $[H_2SO_4]$, as shown in Table 1. When $[H_2SO_4]$ was increased, both wavelength and wave period decreased. Note that, for the same concentrations, the wave period in the unstirred medium was always shorter than the period of oscillation in the well-stirred solutions. This implies that propagating waves suppress self-oscillations of the BZ reaction [22]. The concentration of H_2SO_4 affected the wave velocity in an opposite way as for wavelength and wave period. The wave velocity increased with $[H_2SO_4]$, which agrees well with a previous study [18].

We have presented a study on the bubble-free BZ reaction with substrate pyrogallol, in which its long-term dynamics are not interrupted by bubble formation. The results showed that the behaviour of both the well-stirred solutions and the thin unstirred reactive layers are affected by the concentration of H_2SO_4. The influence of other reagents, i.e., $NaBrO_3$, pyrogallol, or ferroin, would also be interested and is currently under investigation.

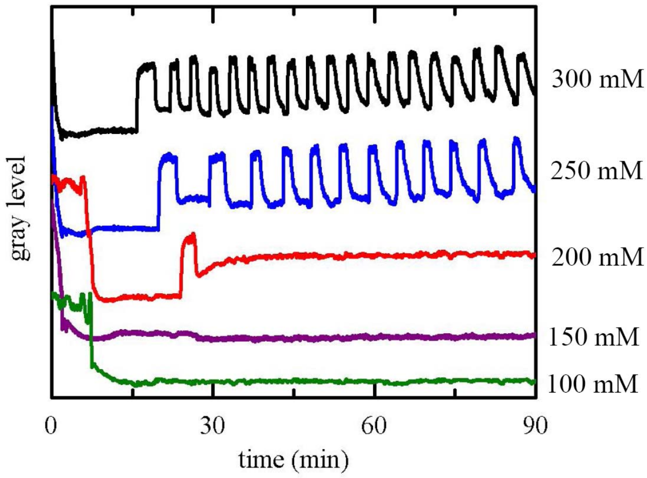

Fig. 2: Dynamics of well-stirred BZ solutions. Bottom to top graphs: $[H_2SO_4]$ = 100, 150, 200, 250, and 300 mM with $[NaBrO_3]$ = 150 mM, [pyrogallol] = 15 mM, and [ferroin] = 0.5 mM in all cases. The graphs were shifted along the ordinate for illustration purposes. The solutions stayed red (low gray level) all the time, when $[H_2SO_4] \leq 150$ mM. At a higher concentration $[H_2SO_4]$ = 200 mM, the colour of the solutions changed to blue (high gray level) for a few minutes, before it turned to red again. For $[H_2SO_4]$ = 250 and 300 mM, the colour of the solutions oscillated between red and blue with a period of about 5.6 and 3.9 min for 250 and 300 mM, respectively.

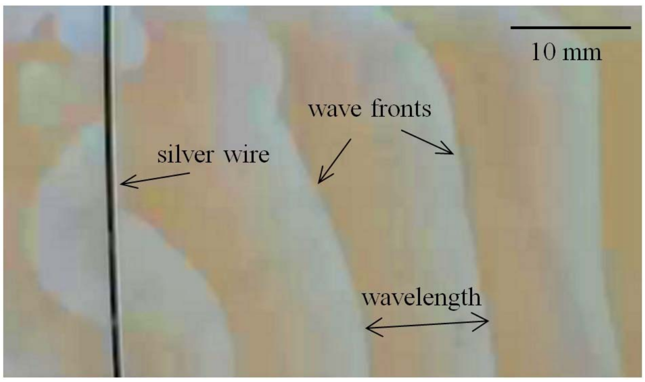

Fig. 3: Propagating waves in an unstirred BZ medium. Initial concentrations: $[H_2SO_4]$ = 150 mM, $[NaBrO_3]$ = 150 mM, [pyrogallol] = 15 mM, and [ferroin] = 0.5 mM. A silver wire was immersed vertically into the flat reactor to induce waves of blue colour travelling on a red background. In the top portion of the image waves from other triggering sources (e.g., dust) occurred and collided with the waves initiated by the silver wire. Wavelength is measured as the distance between two adjacent (almost) planar portions of the wave fronts. Scale bar: 10 mm.

Table 1 Effect of $[H_2SO_4]$ on oscillation period of well-stirred BZ solutions and properties of propagating waves in unstirred BZ media. Other reagents: $[NaBrO_3]$ = 150 mM, [pyrogallol] = 15 mM, and [ferroin] = 0.5 mM.

$[H_2SO_4]$ (mM)	oscillation period (min)	wave period (min)	wavelength (mm)	velocity (mm min^{-1})
100	no oscillation	no wave	no wave	no wave
150	no oscillation	8.7	10.0	1.2
200	no oscillation	5.1	9.1	1.7
250	5.6	3.2	7.7	2.4
300	3.9	2.1	6.2	2.9

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