

Influence of Acidity on Spiral Waves in a Bubble-Free Belousov-Zhabotinsky Reaction with Pyrogallol

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ABSTRACT

Spiral waves are ubiquitously observed in a variety of physical and biological systems, including superconductors, superfluids, CO-oxidation on platinum surfaces, cell aggregation of slime mold and arrhythmia in cardiac tissues. Such spiral waves are uniquely explained by a reaction-diffusion mechanism. Due to easy preparation and convenient detection, the excitable chemical Belousov-Zhabotinsky (BZ) reaction is employed to study spiral waves in experiments. We studied the influence of initial concentration of H_2SO_4 ($[H_2SO_4]$) on the dynamics of spiral waves in a thin layer of the BZ reaction with pyrogallol. This reaction has an advantage over the classical BZ reaction with malonic acid, as it is bubble-free. We found that the spiral tip, i.e., the organizing center, moved along so-called meandering trajectories with three or four outward petals. In addition, the area occupied by the spiral tip decreased when $[H_2SO_4]$ was increased. We further investigated the dynamics far from the organizing center by measuring properties of propagating fronts. An increase of $[H_2SO_4]$ resulted in a simultaneous decrease of the wavelength and wave period. In contrast, the wave speed grew with $[H_2SO_4]$. Since disturbances by the byproduct CO_2 bubbles are avoided and the wave velocity is sufficiently low, the results present a suitable guideline for further investigations on propagating excitation waves in two- and three-dimensional excitable media, especially observations of wave instabilities in three-dimensional systems using optical tomography.

Keywords: Excitable medium, Self-organization, Meander, Tip trajectory.

INTRODUCTION

Spiral waves have been observed in different systems, such as superconductors (de Gennes, 1966), superfluids (Blaauwgeers et al., 2000), CO-oxidation on platinum surfaces (Nettesheim et al., 1993) and cell aggregation of slime mold (Siegert and Weijer, 1989). Spiral waves of electrical excitation and their instabilities are involved in cardiac tachycardia and life-threatening fibrillations of

the heart (Winfrey, 1994; Gray et al., 1998; Fenton et al., 2002). The dynamics of spiral waves are often studied using the Belousov-Zhabotinsky (BZ) reaction as a convenient laboratory model (Zhabotinsky, 1964, Winfree, 1972). Depending on the initial concentrations of reagents, the spiral tip may either rotate simply on a circular path or it may meander, involving a more complicated path of motion (Müller et al., 1985; Plessner et al., 1990; Skinner and Swinney, 1991; Nagy-Ungvarai et al., 1993; Li et al., 1996; Luengviriyaya et al., 2006). However, the classical BZ reaction, with malonic acid as organic substrate, produces CO₂ bubbles that disturb the propagation of waves and their observation (Storb et al., 2003; Luengviriyaya et al., 2008).

We studied the dynamics of spiral waves in a bubble-free BZ reaction, with pyrogallol (1,2,3-trihydroxybenzene) as substrate (Körös et al., 1980; Giles et al., 1992; Orbán et al., 1998; Sridevi and Ramaswamy 1998; Dutt, 2002; Pornprompanya et al., 2002; Pornprompanya et al., 2003). We studied the effect of the initial concentration of H₂SO₄ on the dynamics of the organizing center, as well as the properties of propagating fronts in a thin layer of solution.

MATERIALS AND METHODS

The bubble-free BZ solutions were prepared from NaBrO₃, H₂SO₄, pyrogallol and ferroin, all purchased from Merck. Stock solutions of NaBrO₃ (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 H₂SO₄ (2.5 M) and ferroin (25 mM) were commercially available.

To prevent any hydrodynamic perturbation, the reaction was embedded in a 1.0% w/w agarose gel (Sigma). Appropriate volumes of the stock solutions were mixed and diluted in deionized water to form BZ solutions with different initial concentrations of reagents: [H₂SO₄] was varied between 100 mM and 400 mM, while [NaBrO₃]=150 mM, [pyrogallol]=20 mM and [ferroin]=0.625 mM were fixed in all cases. We investigated the dynamics of spiral waves in a uniform thin layer of the BZ reaction in a flat reactor constructed from transparent plexiglas plates (Luengviriyaya et al., 2006). The medium volume was 100×100×1.0 mm³.

An isolated spiral wave was initiated at about the middle of the medium by the following procedure: The reactor was oriented vertically and 5 ml of BZ solution were filled into the reactor forming the first layer of 5 cm height. Then, we waited until the gel was formed. Wave fronts were initiated by immersion of a silver wire of 0.5 mm diameter close to the left edge of the reactor. Note that the silver wire locally reduces [Br⁻], which is the inhibitor of the system, by forming AgBr. Next, we waited until one open end of the wave front reached the edge of the reactor and the other open end was located near the middle of the reactor. Another 5 ml of the BZ medium were added to the reactor as the second layer. Shortly after filling the second layer, the open end of the wave front started to curl in and began to form an isolated spiral wave in the BZ system.

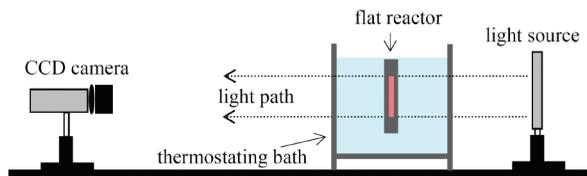


Figure 1. Experimental setup.

The dynamics of the spiral wave was observed in a spectrophotometric setup, as shown in Figure 1. The reactor was placed into a transparent plexiglas bath thermostated at a temperature of $24 \pm 0.1^\circ\text{C}$. The bath was set between a white light source and a color CCD camera (Super-HAD, Sony). To trace the spiral tip precisely, the images of the medium were recorded every second with a resolution of 0.025, 0.033 or 0.050 mm pixel⁻¹.

For analysis, the color images were converted to 8-bit gray scale ones. The contrast of the images was further enhanced by background subtraction and histogram stretching. The background was calculated as the temporal average of all images. The wavelength was measured as the distance between two adjacent fronts. The period was the duration that it took a wave front to travel for a distance of one wavelength. The speed of the wave front was calculated as the ratio between wavelength and period.

The spiral tip was defined as the intersection of contour lines ($0.6 \times$ amplitude) of two subsequent images with a time interval of 5 seconds (Fig. 2a) as proposed in (Grill et al., 1966). A temporal set of the tip positions was plotted to show the tip trajectory (Fig. 2b).

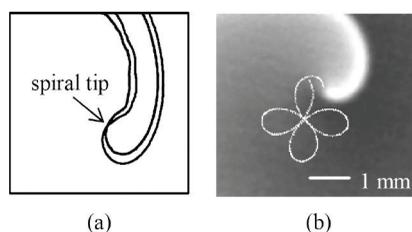


Figure 2. Analysis of spiral tip motion. (a) Definition of the spiral tip. (b) Plot of a spiral tip trajectory.

RESULTS AND DISCUSSION

Our fresh prepared BZ solutions had red color due to the reduced state of ferroin. Our results showed that the dynamics of these BZ media depended on the initial concentration of H_2SO_4 . For moderate concentrations $[\text{H}_2\text{SO}_4] = 150\text{--}300$ mM, the BZ media exhibited propagating spiral waves. The spiral tip (the organizing center of the wave structure) moved along well-known meandering trajectories often found in different excitable media (Müller et al., 1985; Plesser et al., 1990; Skinner, and Swinney, 1991; Nagy-Ungvarai et al., 1993; Li et al.,

1996; Luengviriya, 2006). We observed two types: 3-petal and 4-petal forms of meandering trajectories, as shown in Figure 3. Note that these paths did not remain unchanged. They might slowly translate or/and rotate, as commonly found in other systems.

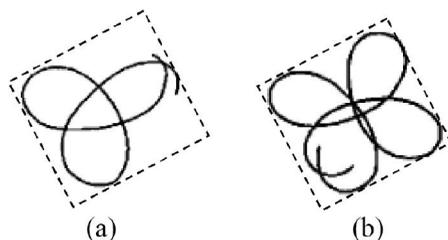


Figure 3. Spiral tip trajectories with (a) 3-petal and (b) 4-petal forms. Dashed rectangles indicate occupying areas of the spiral tip.

Table 1 summarized dynamics of the spiral tip at different $[\text{H}_2\text{SO}_4]$. For low concentration 150 mM, the spiral meandered with 3-petal. As the concentration increased, the trajectory form changed to 4-petal. However, it took the 3-petal shape when the concentration was increased to 275 and 300 mM.

The fate of spiral waves in excitable media generally depends on the motion of the spiral tip. The spiral waves are terminated when the tip strongly meanders and ultimately hits the boundary of the media. To study the strength of the meandering, we measured the occupying area where the spiral tip was located (see Fig. 3). As shown in Table 1, this area monotonously decreased when $[\text{H}_2\text{SO}_4]$ was increased. In addition, it was independent to the form of trajectory.

Table 1. Form and occupying area of the tip trajectory of spiral waves at different $[\text{H}_2\text{SO}_4]$.

$[\text{H}_2\text{SO}_4]$ (mM)	Form	Occupying area (mm^2)
100–125	no wave	no wave
150	3-petal	6.622
175	4-petal	2.85
200	4-petal	2.59
225	4-petal	1.56
250	4-petal	1.44
275	3-petal	1.21
300	3-petal	1.00
325–400	no wave	no wave

For very low concentrations ($[\text{H}_2\text{SO}_4] \leq 125$ mM), the media were unexcitable. Its color stayed red all of the time and waves could not be triggered by a silver wire (marked as “no wave” in Tables 1 and 2). A spiral wave also could not be propagated in the case of very high concentrations ($[\text{H}_2\text{SO}_4] \geq 325$ mM, “no

wave” in Table 1 and 2). Even though waves were initiated, they only survived for a short time and the media changed rapidly from red to blue. In this case, the systems were in a so-called stable oxidized state as reported recently in our article (Luengviriya et al., 2013).

Dynamics of the media far from the spiral tip were investigated via measurements of the properties of wave fronts emitted from the organizing center. As shown in Table 2, when $[H_2SO_4]$ was increased from 150 mM to 300 mM, both the wavelength and wave period of the fronts decreased, while the wave speed grew. The meandering motion of the organizing center acted as a non-stationary source and caused the Doppler effect. The local properties of wave fronts fluctuated over time. The average values are presented, together with the standard deviations, in Table 2.

Table 2. Properties of propagating fronts at different $[H_2SO_4]$. λ : wavelength, T: wave period and v: speed.

$[H_2SO_4]$ (mM)	λ (mm)	T (min)	v (mm min ⁻¹)
100–125	no wave	no wave	no wave
150	8.99±0.86	7.81±1.15	1.16±0.09
175	6.65±0.36	5.55±0.52	1.20±0.06
200	6.03±0.73	4.29±0.77	1.43±0.21
225	5.79±0.56	3.92±0.68	1.50±0.16
250	5.83±0.75	3.62±0.50	1.62±0.07
275	5.98±0.68	3.69±0.27	1.63±0.22
300	5.79±0.75	3.38±0.67	1.76±0.37
325–400	no wave	no wave	no wave

CONCLUSIONS

We have studied the influence of $[H_2SO_4]$ on dynamics of spiral waves in the BZ reaction with pyrogallol. For concentrations $[H_2SO_4] = 150\text{--}300$ mM, the BZ media supported meandering spiral waves. The spiral tip moved along a 3-petal or 4-petal path whose occupying area decreased when $[H_2SO_4]$ was increased. Far from the spiral tip, the front properties were measured. As $[H_2SO_4]$ increased, the wavelength and the wave period decreased, while the wave speed increased.

The media in this investigation are advantageous because they do not produce CO_2 bubbles and they support slow wave propagation. These properties make the present media suitable for further investigations on propagating excitation waves in 2D and 3D excitable media, especially observations of wave instabilities in 3D media using optical tomography (Storb et al., 2003; Luengviriya et al., 2008).

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