

Chemical Wave Studies in the Bromate–Pyrocatechol Beads System

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ABSTRACT: We studied the chemical wave activity of the pyrocatechol-acidic bromate system in the presence of ferroin-loaded beads. The wave activity lasted for more than 24 h while meandering spirals continued for up to 10 h. Rigid and meandering spiral waves were investigated. We have analyzed the wave propagation speed and spiral tip trajectory versus the initial concentrations of all reagents as well as the age of the solution. Wave velocity depends on $[H^+]$ and $[BrO_3^-]$ concentrations by the relationship $v = k[H^+]^{1/2}[BrO_3^-]^{1/2}$, which is in agreement with other studies. This system is ideal to study wave activity and spiral waves as it does not produce precipitates under the studied conditions. © 2011 Wiley Periodicals, Inc. *Int J Chem Kinet* 1–6, 2011

INTRODUCTION

Systems like aggregating slime mold cells, cardiac muscle tissues, chicken retina, the Belousov–Zhabotinsky (BZ) reaction, and CO oxidation on a platinum surface exhibit different types of spatiotemporal patterns [1–15]. Although these are very different systems, the observed wave activities are nevertheless governed by similar reaction-diffusion mechanisms. The first demonstration of propagating waves in autocatalytic chemical systems was reported by Luther about 100 years ago [3]. Spiral waves in a chemical system were first observed in the BZ reaction [2]. In

the past three decades, the BZ reaction has become one of the most widely investigated model systems for studying wave patterns because of its inexpensive compounds, easy preparation process, and easy detectability of wave patterns by applying different catalysts such as ferroin, light-sensitive $Ru(bpy)_3^{2+}$, or $Fe[batho(SO_3)_2]^{4-/3-}$ [16–21]. Müller et al. studied the effect of short light impulses on meandering spiral wave in the BZ reaction with $Ru(bpy)_3^{2+}$ as catalyst and malonic acid as organic substrate [22]. Steinbock et al. also observed meandering spirals in the BZ reaction with 1,4-cyclohexandione (CHD) as an organic substrate and $Fe[batho(SO_3)_2]^{4-/3-}$ as a catalyst [21]. They believed that a long-term rotation period and wavelength of rotations are due to slow relaxation kinetics between catalyst and CHD as well as CHD-derived organic substrates.

According to Steinbock et al., the most important factor determining the characteristics of spiral tip motion is the kinetics of the reaction between the organic substrate and bromate [21]. It is, therefore, interesting to provide examples of meandering spiral waves using

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different organic substrates and/or oxidizing agents. In this study, we investigated the dependence of a spiral tip trajectory on various parameters in the newly discovered pyrocatechol–bromate system [23–25]. This system does not produce gases under the studied conditions and exhibits very long-term chemical wave activity, which makes it an attractive system for further investigation of nonlinear spatiotemporal behaviors such as spiral tip trajectory and anomalous dispersion in two- and three-dimensional media [24].

EXPERIMENTAL

Stock solutions of NaBrO_3 (Aldrich, Mississauga, Ontario, Canada; 99%), 0.6 M, and sulfuric acid (Aldrich; 95–98%), 4.0 M, were prepared with doubly distilled water. Ferroin, 0.025 M, was prepared from a calculated amount of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Aldrich; 99+%) and 1,10-phenanthroline (Aldrich; 99+%). Pyrocatechol (Sigma, Mississauga, Ontario, Canada; 99%) was directly dissolved in the reaction mixture. Samples for chemical wave studies were taken from a 30-mL reaction mixture in a stirred batch reactor at about 30 min after mixing all chemicals together. All chemicals were used in their commercial grade without further purification.

Chemical waves were investigated by spreading the reaction solution mixture onto a thin layer of cation-exchange resin loaded with ferroin. The analytical grade 100–200 mesh ion-exchange resin (Dowex 50W-X4) was purchased from the Fisher Scientific Co. First, 30 g of ion-exchange resin was washed five times with doubly distilled water to modify its acidity [26]. Then it was filtered and used to load ferroin with the desired concentrations. To load the catalyst ferroin onto the resin, filtered resin was mixed with ferroin solution (30 mL of 0.002 M, unless otherwise mentioned in the text) and the mixture was stirred vigorously at 600 rpm overnight. The ferroin solution became transparent at the end of the process, presumably due to the complete absorption of ferroin by the cation beads. The mixture was left unstirred for 30 min, and then we removed solution on top of the beads. Ferroin-loaded beads were washed three more times through adding 60 mL of doubly distilled water and stirring for 10 min each time. This washing is useful in removing imperfect beads and any impurities. It is also beneficial in reducing the amount of beads floating on the top of reaction mixture in the Petri dish.

To begin our experiments, 22.5 mL of the reaction mixture was mixed with 3.0 (± 0.1) g of the beads loaded with ferroin in a Petri dish (9 cm in diameter), in which the beads formed a thin film of 0.3 (± 0.1) mm

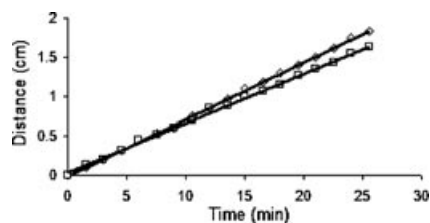


Figure 1 Wave propagation speed under reaction conditions: $[\text{bromate}] = 0.068 \text{ M}$, $[\text{acid}] = 1.40 \text{ M}$, $[\text{pyrocatechol}] = 0.035 \text{ M}$, $[\text{ferroin}] = 0.002 \text{ M}$, and 3.0 g of beads; wave speed was calculated at (\diamond) 200 min and (\square) 450 min after the appearance of wave activity.

on the bottom of the Petri dish. The Petri dish was maintained at room temperature of $20 \pm 1^\circ\text{C}$. Confirming spiral tip movement and anomalous behavior, some of the experiments were repeated several times. The evolution of the spatially extended medium was monitored with a CCD camera equipped with a zoom lens. The CCD camera was connected to a personal computer running a frame grabber program (Matrox Imaging Library). Images were stored on an external hard disk for future analysis. The tip position of a spiral was determined visually and was checked several times for accuracy assurance.

RESULTS AND DISCUSSION

The propagation speed of the target waves in ferroin-loaded cationic beads was analyzed at different stages, e.g., the initial stage during which waves just emerged, and the later stage from 100 to 600 min after spreading the reaction mixture in the Petri dish. Figure 1 characterizes the propagation speed of the waves between 200 and 450 min; the spatial location of a wave segment is plotted versus time. Linearity of these curves indicates a constant wave velocity, independent of time or curvature of the band in a short period of time. The velocity of successive waves slightly decreases in time because of reactant consumption. This plot shows that wave propagates at average rates of 0.07 and 0.06 cm/min at 200 and 450 min, respectively. The decline in wave speed is due to the aging of the reaction mixture. However, within a short time frame, the wave speed is almost constant. The decrease in wave propagation speed as times goes on is one of the common aspects of the closed reaction system. While in most conditions studied here chemical waves last between 600 and 800 min, in some conditions they lasted for up to 1300 min. In this study, the analysis of chemical wave speed was done 200 min after the first appearance of wave activity in the Petri dish.

The dependence of wave velocity on the initial concentrations of different reagents is shown in Fig. 2. This

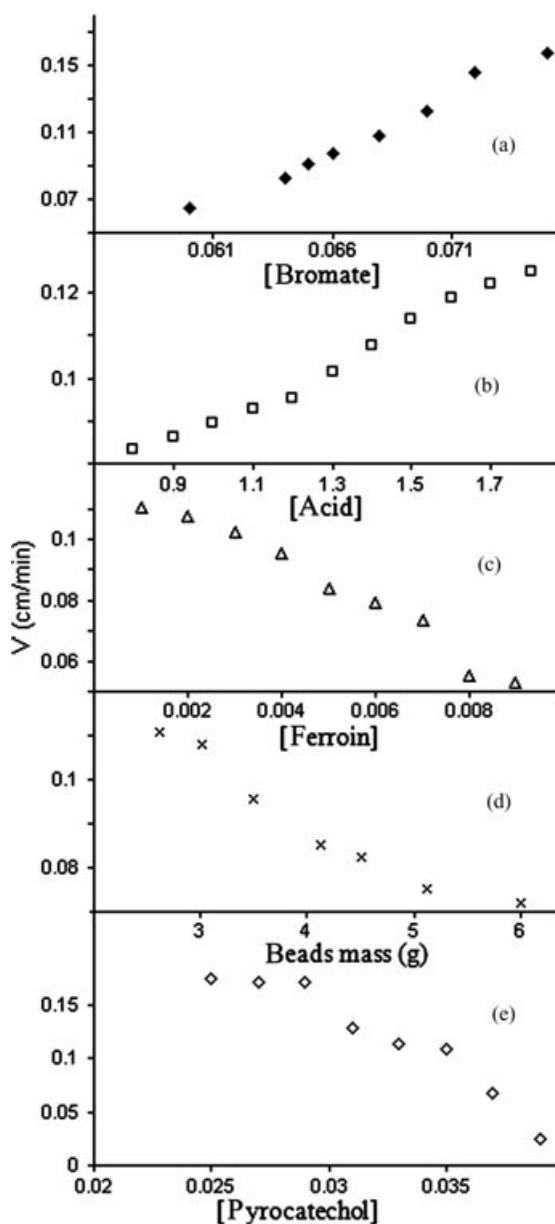


Figure 2 Wave propagation speed versus (a) initial bromate concentration while other reagent concentrations were fixed at [acid] = 1.40 M, [pyrocatechol] = 0.035 M, [ferriin] = 0.002 M, and 3.0 g of beads; (b) initial acid concentration while other reagent concentrations were fixed at [bromate] = 0.068 M, [pyrocatechol] = 0.035 M, [ferriin] = 0.002 M, and 3.0 g of beads; (c) initial ferriin concentration while other reagent concentrations were fixed at [bromate] = 0.068 M, [acid] = 1.40 M, [pyrocatechol] = 0.035 M, and 3.0 g of beads; and (d) beads mass while other reagent concentrations were fixed at [bromate] = 0.068 M, [acid] = 1.40 M, [pyrocatechol] = 0.035 M, [ferriin] = 0.002 M; (e) initial pyrocatechol concentration while other reagent concentrations were fixed at [acid] = 1.40 M, [bromate] = 0.068 M, [ferriin] = 0.002 M, and 3.0 g of beads. Wave speed analyses were done 200 min after the appearance of wave activity in all cases.

figure shows that a higher amount of beads mass causes a decrease in wave velocity. As is demonstrated in part (a) of this figure, the propagation speed increases with increasing bromate concentration. At high concentration of bromate (>0.075 M), the visibility of these waves was not good and when the concentration of bromate was larger than 0.08 M the system did not exhibit any wave activity. When the concentration of bromate is higher than 0.072 M, the system exhibited target and spiral waves. Although wave activity had a better contrast at low bromate concentration, it lasted for a shorter period of time.

The acid concentration effect on wave propagation speed is shown in Fig. 2b. An increase in acid concentration from 0.8 to 1.8 M raised the wave propagation speed from 0.08 to 1.25 cm/min. Again, in all cases the rate was measured at 200 min after the initial appearance of wave activity in the medium. Higher acid concentration (≥ 1.6 M) resulted in poor differentiation between wave and background color, and therefore it was difficult to carry out an accurate analysis, but this allowed wave activity to survive for a longer period. At low acid concentration, i.e., lower than 1.2 M, this system showed only target waves. Studies on the effect of initial concentration of ferriin loaded onto ion-exchange resins were also carried out; the result of this study is presented in Fig. 2c, which illustrates the change in wave propagation speed versus ferriin concentration. According to Fig. 2c, increasing ferriin concentration causes a decrease in wave propagation speed. However, in the classic BZ and CHD-BZ reaction, the wave speed is typically independent of the catalyst concentration. In this system, pyrocatechol and ferriin buildup coupled autocatalytic feedbacks, which can be a source of this extraordinary behavior [25]. To test the effect of ferriin concentration, concentrations of bromate and acid and the mass of beads were kept constant at 0.068 M, 1.4 M, and 3.0 g, respectively. Carrying out preliminary studies on beads mass effect on chemical wave activity, we kept acid and bromate concentrations constant at 1.4 and 0.068 M, respectively. Figure 2d plots wave propagation speed as a function of beads mass, in which wave speed decreases as beads mass increases from 2.6 to 6.0 g. Such a result is consistent with the effect of ferriin concentration on the wave propagation rate.

Figure 3a shows evolution of spiral tip movement (meandering and rigid) with time versus initial bromate concentration. The movement of the spiral tip can be classified into a diversity of qualitatively different trajectories including cycloidal curves and simple circles. These behaviors are referred to as meandering and rigid rotation, respectively. When the bromate concentration is equal to or less than 0.065 M, the system yields rigid

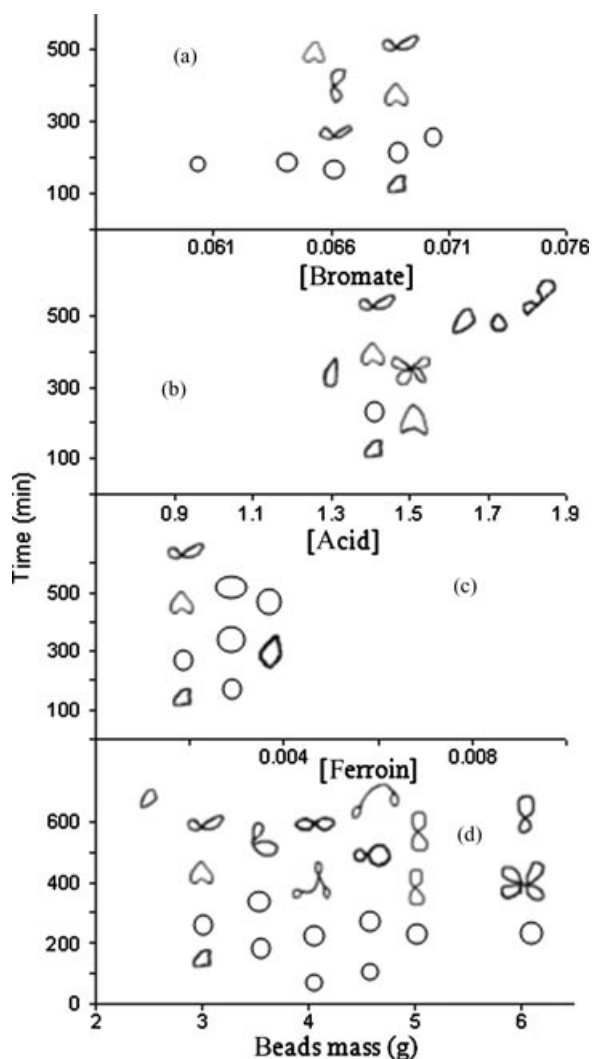


Figure 3 Spiral tip trajectory versus (a) initial bromate concentration while other reagent concentrations were fixed at [acid] = 1.40 M, [pyrocatechol] = 0.035 M, [ferroin] = 0.002 M, and 3.0 g of beads; (b) initial acid concentration while other reagent concentrations were fixed at [bromate] = 0.068 M, [pyrocatechol] = 0.035 M, [ferroin] = 0.002 M, and 3.0 g of beads; (c) initial ferroin concentration while other reagent concentrations were fixed at [bromate] = 0.068 M, [acid] = 1.40 M, [pyrocatechol] = 0.035 M, and 3.0 g of beads; and (d) beads mass while other reagent concentrations were fixed at [bromate] = 0.068 M, [acid] = 1.40 M, [pyrocatechol] = 0.035 M, and [ferroin] = 0.002 M.

spiral tip movement. On the other hand, at high bromate concentrations the medium exhibits meandering spiral tip as well. Notably, as shown in Fig. 3, the motion of these spiral tips changes with time, because chemicals are consumed continuously, which consequently alternate the dynamics of the reaction medium. The greatest variety of chemical wave activities was ob-

served when the bromate concentration was between 0.066 and 0.070 M. The system exhibited two stages of wave breakup: the first one was the breakup of circular wave to spiral; subsequently, spirals fell apart from outside toward inside, forming lots of wave segments. The process of spiral segmentation always starts from the outer spiral's tail (see Fig. 4). Furthermore, Fig. 4 exhibits a very interesting phenomenon in which the wavelength of a single spiral wave is much shorter than that of the other waves. Therefore, the area occupied by this single spiral increases with time because of its faster dynamics. But somehow this spiral slows down and growth stops. This is a common scenario between 0.066 and 0.070 M of bromate where the acid concentration is between 1.30 and 1.50 M. Please note that this is a closed system where no fresh chemicals are supplied. It is possible to have a single spiral in the whole Petri dish if the single spiral can keep its faster pace for a longer time, probably through running the experiment in a continuously fed unstirred reactor.

The acid concentration effect on the spiral tip trajectory is shown in Fig. 3b. When the acid concentration was higher than 1.3 M, the system was able to exhibit spirals with meandering or rigid tip movement. When the acid concentration was 1.5 M, the trajectory of the tip looked like a hypocycloid. This complex route can be considered as a superposition of two circular motions with different radii and rotational frequencies in contrast to a rigid rotation where the tip rotates with a constant frequency on a circular pathway with a fixed center [21]. Quantitative analysis of the data reveals an increase in the number of petals as the concentration of acid is increased.

Results of the ferroin concentration effect on the motion of spirals are presented in Fig. 3c. For the concentration of ferroin between 0.003 and 0.004 M, the reaction-diffusion medium supports a rigidly rotating spiral wave for at least 6 h. During this time, the size of the spiral core expanded. When the ferroin concentration is higher than 0.005 M, the system exhibits just target waves with an anomalous dispersion behavior. At a low concentration of ferroin, 0.001 M, there are plenty of wave activities in the system such as anomalous dispersion and spiral tip movement; however, due to a visibility dilemma we were not able to follow spiral tip trajectory.

Figure 3d shows the spiral wave tip trajectory as a function of beads mass, where beads mass was adjusted between 2.6 and 6.0 g. High beads mass was in favor of meandering spiral. At lower beads mass, meandering spiral occurred at a later stage of wave activity, whereas at high beads mass meandering behavior appeared in earlier stages and lasted over 10 h, until the end of wave activity. Another phenomenon that this system is able

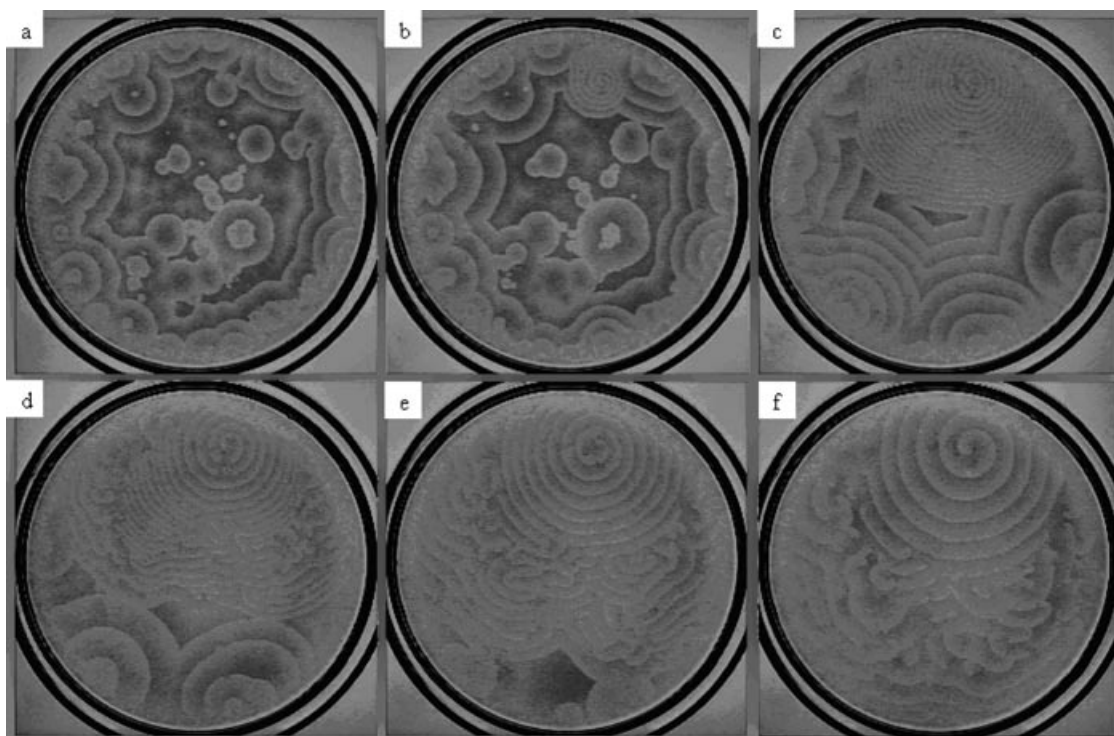


Figure 4 Chemical waves at 60 (a), 70 (b), 110 (c), 150 (d), 200 (e), and 262 (f) min. In panel (a) circular wave breaks up to form spirals. In panel (c), the spiral starts breaking up from its tail. Other reaction conditions are [bromate] = 0.068 M, [acid] = 1.40 M, [pyrocatechol] = 0.035 M, [ferroin] = 0.002 M, and 3.0 g of beads.

to support at beads mass higher than 3.5 g is anomalous dispersion. According to experimental studies by Steinbock et al. [21], anomalous dispersion happens because waves propagate faster at the beginning and then they propagate slower, which makes wave trains having different distances in different areas. Another observed phenomenon was the meandering movement of the spiral tip in the beads–pyrocatechol system as the distance between waves increased on one side and

decreased on the other side of the spiral (closer in the direction of tip movement) because of the meandering movement of the spiral tip (an example is shown in Fig. 5) [27]. In the described chemical medium, spiral waves exist for more than 10 h, during which the size of this meandering pattern increases slowly with the aging of the solution.

As observed in earlier studies [26–29], the wave propagation velocity in the BZ reaction is strongly

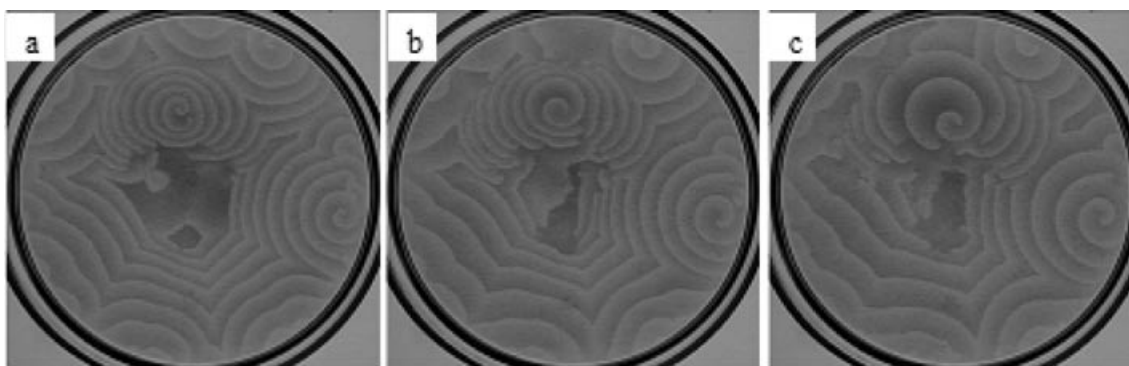


Figure 5 (a) Appearance of meandering spiral that with tip movement causes anomalous behavior in system 254 (a), 308 (b), and 408 (c) min. Other reaction conditions are [bromate] = 0.068 M, [acid] = 1.40 M, [pyrocatechol] = 0.035 M, [ferroin] = 0.002 M, and 6.0 g of beads.

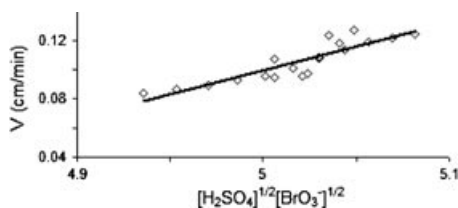


Figure 6 Plot of velocity of band propagation versus square root of product of initial concentrations of acid and sodium bromate: [pyrocatechol] = 0.035 M, [ferroin] = 0.002 M, and 3.0 g of beads.

dependent on the initial concentrations of sulfuric acid and sodium bromate. The form of the concentration dependence on sulfuric acid and sodium bromate is characterized to be the square root of the product of their initial concentrations. For this reason, our results are represented in this form. A linear dependence of wave velocity on the product $[H^+]^{1/2}[BrO_3^-]^{1/2}$ is shown in Fig. 6. The best two-parameter least-squares line through the points is

$$V(\text{cm/min}) = 0.4959 \times [H^+]^{1/2}[BrO_3^-]^{1/2} - 0.0445 \quad (1)$$

CONCLUSIONS

We report preliminary experimental results of the chemical wave activity in the pyrocatechol–bromate system spread in the ferroin-loaded beads. Variation of wave propagation speed and spiral tip trajectory versus four different factors including concentration of bromate, acid, and ferroin and beads mass was characterized. Depending on the reaction conditions, this system exhibits a variety of concentration patterns with a long lifetime for up to 24 h on average. High concentrations of acid and bromate are generally in favor of longer chemical wave activity but not in favor of image contrast. Therefore, following the motion of a spiral tip at high concentration of these two reagents is a challenging issue. In the studied system, spiral tips exhibit both rigid and meandering movements for up to 10 h. Chemical wave speed increases with increasing acid and bromate concentration but decreases with the concentration of ferroin and mass of beads. This system needs more investigation on the influence of light and/or laser pulses on spiral tip movement. Also, according to our preliminary studies, spiral tip movement speed changes during the reaction lifespan, which will be a topic of more investigations in future.

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