MECHANISM FOR THE COLOR TRANSITION OF THE
BELOUSOV–ZHABOTINSKY REACTION CATALYZED BY
CERIUM IONS AND FERROIN

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Abstract. The oscillation property of the Belousov–Zhabotinsky reaction and the color transition of its solution depend on the catalytic action of the metal ions. The solution of the reaction system catalyzed by both cerium ions and ferroin has a more complicated effect on the color than either the cerium-catalyzed case or the ferroin-catalyzed case. To theoretically elucidate the color transition of the case catalyzed by these two ions, a reduced model consisting of three differential equations is proposed, incorporating both the Rovinsky–Zhabotinsky scheme and the Field–Körös–Noyes scheme simplified by Tyson [Ann. N.Y. Acad. Sci., 316 (1979), pp.279–295]. The presented model can have a limit cycle under reasonable conditions through a Hopf bifurcation, and its existence theorem is proven by employing the bifurcation criterion established by Liu [J. Math. Anal. Appl., 182 (1994), pp.250–256].

1. Introduction. Since its discovery in 1958, the Belousov–Zhabotinsky (BZ) reaction, a typical chemical oscillation, has been variously studied in the areas of physics, chemistry, and mathematics. Quantitative data of the rhythmic phenomenon of the BZ reaction can be gained by continuously monitoring the redox potential (oxidation–reduction potential: ORP) of the adequately stirred solution. On the other hand, by leaving the thinly stretched solution of the BZ reaction in a petri dish, it is possible to observe the time evolution of target and spiral patterns. This study deals with the rhythmic phenomenon.

Field, Körös, and Noyes (FKN) elucidated the essential mechanism of the BZ reaction in their celebrated work [3]. Since then, many articles have been published, proposing the detailed reaction mechanism from experimental and thermodynamic points of view. In particular, we refer readers to studies by Field and Försterling [2], Försterling et al. [5], Györgyi and Field [6, 7], Györgyi et al. [8], and Kshirsagar and Field [10] as the key reports directly concerning the topic of the present paper. The Oregonator established by Field and Noyes [4] is a mathematical model of three ordinary differential equations that describes the FKN mechanism on the basis of the chemical kinetics. The Oregonator is a well-known limit cycle oscillator.

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The BZ reaction is a self-motivated repetition of oxidation–reduction reactions generated by mixing an oxidant, a reductant (substrate), a strong acid, and a metal ion catalyst. The type of catalyst used affects the oscillatory property. Cerium ions are usually adopted as a catalyst for experiments on rhythmic phenomena, whereas ferroin is used for the pattern formulation. The reason for this is the fact that oscillations generated by ferroin-catalyzed systems have higher frequencies and more vivid color transitions than cerium-catalyzed systems. Depending on the oxidation state of the catalyst, the solution will be yellow/colorless for the couple of $\text{Ce}^{4+}/\text{Ce}^{3+}$ and slightly blue/red for the couple of $\text{Fe(phen)}^{3+}/\text{Fe(phen)}^{2+}$, colors that are distinct enough to be used for a redox indicator.

The color of the solution catalyzed by both cerium ions and ferroin repeatedly changes, with roughly six phases of four colors, as shown in Figure 2. Sjøgren et al. [13] published a brief experimental report on ORP oscillation and the color transition of a cerium–ferroin-catalyzed system. The main purpose of the current paper is to provide a theoretical proof for such a color transition.

From the viewpoint of mathematical modeling, the original Oregonator was purely a cerium-catalyzed system; however, it failed to describe the waveform of the oscillations accurately. Tyson [15] suggested a two-variable reduced model inheriting the dynamical property of the Oregonator. Regardless of the type of catalyst, the Tyson model has been adopted for the theoretical analysis of pattern dynamics using reaction–diffusion equations (refer to [9], [17], and subsequent works). Rovinsky and Zhabotinsky (RZ) [12] developed a reasonable model to show the waveform of ferroin-catalyzed systems. The RZ model is often the basis for physicochemical studies designed to improve the model accuracy with experiments and simulations.

Several enhanced models for single-catalyzed systems were reported to switch between cerium-catalyzed and ferroin-catalyzed systems on adjustment of the concentrations and rate constants (see e.g. [18]). However, the existing models cannot explain the reason for the color transition of cerium–ferroin-catalyzed systems because the simultaneous catalytic action of cerium ions and ferroin cannot be equated to moderate action by a single ion. Our goal is therefore to build and analyze a model that includes the concentrations of both cerium ions and ferroin. To avoid unnecessary complexity of the model, this study lowers the priority of accurately describing the waveform of the cerium–ferroin-catalyzed system.

This paper is organized as follows. In Section 2, we derive the three-variable model for the cerium–ferroin-catalyzed system integrating the Tyson model into the RZ model. Sections 3 and 4 are devoted to explaining the relation between the ORP waveform and the six-phase color transition of the four colors through a comparison of the experimental data and the numerical simulation for our model. In Section 5, a Hopf bifurcation theorem is established for our model by employing Liu’s theorem [11], which is a criterion for simple Hopf bifurcation, given by combining Hopf’s theorem with the Routh–Hurwitz stability criterion. A limit cycle generated by a Hopf bifurcation represents the theoretical elucidation for the periodic color transition. Section 6 illustrates our theorems with three bifurcation diagrams. In Section 7, our conclusions and future problems are stated. For the reader’s convenience, we introduce Liu’s theorem in the Appendix.

2. Mechanism and model. The Oregonator derived from the FKN mechanism models the BZ reaction of a bromate–cerium–bromomalonic/malonic acid system. For the case in which ferroin is used instead of cerium ions as the metal ion catalyst, the substitution of ferroin/ferrin for the cerous/ceric ions does not apply
for the scheme of the BZ reaction. In some studies [2, 12, 14, 18], it was pointed out that the reaction pathway of a ferroin-catalyzed system differs from that of a cerium-catalyzed system because of differences in standard redox potentials of the $\text{Ce}^{4+}/\text{Ce}^{3+}$ and $\text{Fe(phen)}_{3}^{3+}/\text{Fe(phen)}_{2}^{2+}$ couples. The RZ scheme [12] is therefore a modified FKN scheme for a ferroin-catalyzed system.

The scheme of a cerium–ferroin-catalyzed system consists of the following eleven steps selected from the combination of the RZ scheme and the FKN scheme:

1. $\text{H}^{+} + \text{HBrO}_3 + \text{HBrO}_2 \rightleftharpoons \text{HBrO}_2^+ + \text{Br}_2 + \text{H}_2\text{O}$ (R1)
2. $\text{BrO}_2^- + \text{H}^+ \rightleftharpoons \text{HBrO}_2^+$ (R2)
3. $\text{Fe(phen)}_2^{3+} + \text{HBrO}_2^+ \rightleftharpoons \text{Fe(phen)}_3^{3+} + \text{HBrO}_2$ (R3)
4. $\text{Ce}^{3+} + \text{H}^+ + \text{BrO}_2^- \rightleftharpoons \text{Ce}^{4+} + \text{HBrO}_2$ (R4)
5. $2\text{HBrO}_2 \rightleftharpoons \text{HOBr} + \text{HBrO}_3$ (R5)
6. $\text{H}^+ + \text{Br}^- + \text{HBrO}_2 \rightleftharpoons 2\text{HOBr}$ (R6)
7. $\text{H}^+ + \text{Br}^- + \text{HOBr} \rightleftharpoons \text{Br}_2 + \text{H}_2\text{O}$ (R7)
8. $\text{H}^+ + \text{Br}^- + \text{HBrO}_3 \rightleftharpoons \text{HBrO}_2 + \text{HOBr}$ (R8)
9. $\text{Fe(phen)}_3^{3+} + \text{CHBr(COOH)}_2 \rightleftharpoons \text{Fe(phen)}_3^{2+} + \cdot \text{CBr(COOH)}_2 + \text{H}^+$ (R9)
10. $\cdot \text{CBr(COOH)}_2 + \text{H}_2\text{O} \rightleftharpoons \cdot \text{COH(COOH)}_2 + \text{Br}^- + \text{H}^+$ (R10)
11. $4\text{Ce}^{4+} + \text{CHBr(COOH)}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{Ce}^{3+} + \text{HCOOH} + \text{Br}^- + 2\text{CO}_2 + 5\text{H}^+$ (R11)

Steps (R1), (R2), (R3), (R9), and (R10) are chosen from the RZ scheme; steps (R4) and (R11) are chosen from the original FKN scheme; and steps (R5), (R6), (R7), and (R8) are common to both schemes. This scheme does not involve unknown details of the reactions of organic compounds. Briefly, to characterize the difference between the ferroin-catalyzed system and the cerium-catalyzed system, step (R9) is essentially reversible for the ferrin/ferroin couple, whereas the single-step (R11) is assumed for the ceric/cerous ion couple.

We use the following notations for the reactant concentrations:

- $X = [\text{HBrO}_2]$,
- $Y = [\text{Ce}^{4+}]$,
- $Z = [\text{Fe(phen)}_3^{3+}]$,
- $P = [\text{Br}^-]$,
- $Q = [\text{HBrO}_2^+]$,
- $R = [\cdot \text{CBr(COOH)}_2]$,
- $A = [\text{HBrO}_3]$,
- $B = [\text{CHBr(COOH)}_2]$,
- $C = [\text{Ce}^{3+}] + [\text{Ce}^{4+}]$,
- $F = [\text{Fe(phen)}_2^{3+}] + [\text{Fe(phen)}_3^{3+}]$,
- $H = [\text{H}^+]$.

We also use $k_+$ and $k_-$ to denote the rate constants of the forward and reverse reactions of (Rn), respectively. Letting $X$, $Y$, $Z$, $P$, $Q$, and $R$ represent intermediate products, and employing the following assumptions adopted by Field and Noyes [4], Györgyi et al. [8], Rovinsky and Zhabotinsky [12], and Zhabotinsky et al. [18]:

- The equilibrium in (R2) is shifted almost completely to the right, that is, $[\text{HBrO}_2^+]$ substitutes for $[\text{BrO}_2^-]$.
- HOBr and Br$_2$ are rapidly removed through (R5), (R6), (R7), and (R8).
- For (R9) and (R10), the rate of Br$^-$ production caused by the ferrin reduction is accounted for by the stoichiometric factor $q$. In a similar manner, the rate of Br$^-$ production caused by the reduction of ceric ions through (R11) is accounted for by the stoichiometric factor $r$. See also [14] and [16].
Under these assumptions, we develop the system of rate equations as follows:

\[
\begin{align*}
\frac{dX}{dt} &= -k_1 HAX + k_{-1} Q^2 + k_3 Q(F - Z) - k_{-3} XZ \\
&\quad + k_3 HQ(C - Y) - k_{-4} XY - 2k_5 X^2 - k_6 HXP + k_8 HAP, \\
\frac{dY}{dt} &= k_4 HQ(C - Y) - k_{-4} XY - k_{11} BY, \\
\frac{dZ}{dt} &= k_3 Q(F - Z) - k_{-3} XZ - k_9 BZ + k_{-9} H(F - Z)R, \\
\frac{dP}{dt} &= -k_6 HXP - k_8 HAP + qk_{10} R + rk_{11} BY, \\
\frac{dQ}{dt} &= 2k_1 HAX - 2k_{-1} Q^2 - k_3 Q(F - Z) \\
&\quad + k_{-3} XZ - k_4 HQ(C - Y) + k_{-4} XY, \\
\frac{dR}{dt} &= k_9 BZ - k_{-9} H(F - Z)R - k_{10} R.
\end{align*}
\]

Taking into account the following chemical facts pointed out in [12]:

- \(k_5 \gg k_{-5}\) and \(k_{-9} \gg k_{10} \gg k_9\),
- The concentration of \(\text{HBrO}_2^+\) remains sufficiently small, namely, \(k_{-1} Q^2 \simeq 0\),

and applying the quasi-steady-state approximation to \(P, Q,\) and \(R,\) we obtain a three-variable model as follows:

\[
\begin{align*}
\xi_1 \frac{dy}{dt} &= x(1 + \beta_2 z) - \alpha_1 y - \frac{x(1 + \beta_1 y + \beta_2 z)}{(1 - z) + \eta(1 - y)}(1 - z), \\
\xi_2 \frac{dz}{dt} &= x(1 + \beta_1 y) - \frac{\alpha_2 z}{1 - z} - \frac{x(1 + \beta_1 y + \beta_2 z)}{(1 - z) + \eta(1 - y)}\eta(1 - y).
\end{align*}
\]

where

\[
\begin{align*}
x &= \frac{2k_5}{k_1 H} X, & y &= \frac{Y}{C}, & z &= \frac{Z}{F}, & \tau &= \frac{k_1^2 H^2 A}{k_5 l}, & \varepsilon &= \frac{k_1 H}{k_5}, \\
\xi_1 &= \frac{C}{A}, & \xi_2 &= \frac{F}{A}, & \mu &= \frac{2k_5 k_8}{k_1 k_6 H}, & \eta &= \frac{k_4 H C}{k_3 F}, & K &= \frac{k_9 k_{10}}{k_{-9}}, \\
\alpha_1 &= \frac{k_5 k_{11} BC}{k_1^2 H^2 A^2}, & \alpha_2 &= \frac{k_5 BK}{k_1^2 H^3 A^2}, & \beta_1 &= \frac{k_{-4} C}{2k_1 H A}, & \beta_2 &= \frac{k_{-3} F}{2k_1 H A}.
\end{align*}
\]

All the parameters are positive. In particular, the kinetic reasons allow for \(\mu < 1\).

As was indicated in the studies by Försterling [5], Rovinsky and Zhabotinsky [12], and Zhabotinsky et al. [18], throughout this paper we suppose that

\[
r = 0.5 \quad \text{and} \quad q = 0.5.
\]

The domain for \((\text{CF})\) is

\[
\Omega = \{(x, y, z) \in \mathbb{R}^3 : x \geq 0, \ 0 \leq y < 1, \ 0 \leq z < 1\}.
\]

We remark that system \((\text{CF})\) is a hybrid model of the Tyson model and the RZ model. Provided \(F \to 0\) for the cerium-catalyzed case, then \(\xi_2 \to 0, \eta \to \infty,\) and
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\[ \beta_2 \to 0, \text{ so that (CF) corresponds to the Tyson model of the form} \]
\[
\begin{align*}
\varepsilon \frac{dx}{d\tau} &= x(1 - x) - 2r \alpha_1 y \frac{x - \mu}{x + \mu}, \\
\xi_1 \frac{dy}{d\tau} &= x - \alpha_1 y.
\end{align*}
\]

(T)

On the other hand, if \( C \to 0, \text{ then } \xi_1 \to 0, \eta \to 0, \alpha_1 \to 0, \text{ and } \beta_1 \to 0, \text{ in which case it follows that (CF) corresponds to the RZ model of the form} \]
\[
\begin{align*}
\varepsilon \frac{dx}{d\tau} &= x(1 - x) - 2q \frac{\alpha_2 z}{1 - z} \frac{x - \mu}{x + \mu}, \\
\xi_2 \frac{dz}{d\tau} &= x - \frac{\alpha_2 z}{1 - z}.
\end{align*}
\]

(RZ)

3. **Experimental section.** In terms of chemical phenomena, this section illustrates the difference in oscillation properties between the cerium-, ferroin-, and cerium–ferroin-catalyzed BZ reactions. We also show the color transitions of the cerium–ferroin-catalyzed system with photographic images.

The solutions were prepared for this study as shown in Table 1, and then Exp. I, II, and III were carried out by means of sufficient stirring of the mixtures shown in Table 2 in a 100 mL beaker on a magnetic stirrer hot-plate. The reaction temperature was kept constant at 30\(^\circ\)C. The redox potential of the mixture was measured by using a pH/ORP meter (HORIBA, D-52) with a combination electrode (HORIBA, 9300-10D) composed of a Pt wire and Ag/AgCl electrode immersed in a saturated KCl aqueous solution.

The measured potential, \( E_m \) [mV], is converted to an ORP potential, \( E_{\text{ORP}} \), relative to a standard hydrogen electrode (SHE) with the aid of the relation
\[
E_{\text{ORP}} = E_m + 206 - 0.7(T - 25) \text{ [mV] (vs. SHE)},
\]
where the temperature \( T = 30 \text{ [\degree C]} \).

Figure 1 shows the time sequences of the redox potentials measured five minutes after mixing the solutions to the reading of the steady waveforms. The amplitudes of Exp. I, II, and III were respectively 130, 50, and 245 mV. The period of Exp.
II was approximately 15 s. The periods of both Exp. I and III seemed to be approximately 55 s in the figure, whereas the period of Exp. III was found to be a few percent smaller than that of Exp. I according to a longer measurement time. The important point is that the reaction of Exp. III corresponds to that of Exp. I with a low-dose of ferroin; nevertheless, the oscillation properties clearly differ between Exp. I and III.

Figure 2 shows the cycle of the color transition of Exp. III. Judging visually, the color gradually changes in six phases of four colors: red - purple - blue - green - blue - purple. The solution takes on a deep red at the lowest point on the redox potential curve. The sequence of purple - blue - green is instantaneous, whereas that of blue - purple - red is relatively gentle.

Figure 1. Redox potential curves recorded by the three catalytic types of BZ reactions.

$E_{\text{ORP}}$: 1135 · · · 1333 1362 1218 1178 [mV]

Figure 2. Periodic color transition of the BZ reaction solution (Exp. III) catalyzed by cerium ions and ferroin. The value of $E_{\text{ORP}}$ shows the redox potential of solution at the moment the image was captured.

4. **Numerical simulation.** This section is devoted to the analysis of the reason for the color transition of the cerium–ferroin-catalyzed BZ reaction. We also discuss the adequacy of the (CF) model with the aid of numerical simulation.

For the simulation, we set the parameters as shown in Table 3, the values of which are based on the experimental conditions and ref.[12] except as noted here. For 1M H$_2$SO$_4$, $H = 1.29$ was adopted in [8]. The values of $k_4$ and $k_{-4}$ were ensured at 20°C in [2]. The value of $k_{11}$ was estimated to be 0.4 in [15], 0.4 at 20°C and 0.8 at 40°C in [18], and in the range of 0.5 to 1.0 in [6].
Table 3. Fixed concentrations and rate constants for (T), (RZ), and (CF).

| Concentration | Rate constant |
|---------------|---------------|
|               | $k_1$         | $k_2$          | $k_3$          | $k_4$          | $k_5$          |
| $A$           | 0.04 M        | 100 M$^{-2}$s$^{-1}$ | 10 M$^{-1}$s$^{-1}$ | 10$^3$ M$^{-1}$s$^{-1}$ | 1.7 $\times$ 10$^4$ M$^{-1}$s$^{-1}$ |
| $B$           | 0.10 M        | 8.0 $\times$ 10$^4$ M$^{-2}$s$^{-1}$ | 8.9 $\times$ 10$^3$ M$^{-1}$s$^{-1}$ | 8.0 $\times$ 10$^4$ M$^{-2}$s$^{-1}$ |
| $C$ (Exp. I, III) | 6.3 mM      | 10$^3$ M$^{-1}$s$^{-1}$ | 10$^3$ M$^{-1}$s$^{-1}$ | 10$^3$ M$^{-1}$s$^{-1}$ | 0.8 M$^{-1}$s$^{-1}$ |
| $F$ (Exp. II) | 0.13 mM       | $k_2$          | $k_3$          | $k_4$          | $k_5$          |
| $F$ (Exp. III) | 0.65 mM      | 10$^3$ M$^{-1}$s$^{-1}$ | 10$^3$ M$^{-1}$s$^{-1}$ | 10$^3$ M$^{-1}$s$^{-1}$ | 10$^3$ M$^{-1}$s$^{-1}$ |
| $H$           | 1.29 M        | $k_2$          | $k_3$          | $k_4$          | $k_5$          |

The redox potential, $E_{\text{ORP}}$, for the solution including a single redox couple, $M_{\text{ox}}/M_{\text{red}}$, with the electron transfer reaction $M_{\text{ox}} + ne^- \rightleftharpoons M_{\text{red}}$ is given by Nernst’s equation of the form

$$E_{\text{ORP}} = E^\circ + \frac{RT}{nF} \ln \left( \frac{[M_{\text{ox}}]}{[M_{\text{red}}]} \right)$$

where $R$ is the universal gas constant, $T$ the temperature in Kelvin, and $F$ the Faraday constant. For the case of $n = 1$ at the experimental temperature 30°C given in Section 3, $RT/(nF) = 0.0261$. In addition, $E^\circ$ is the standard redox potential, which depends on the redox couple, the temperature, and the measuring electrode. It is known that $E^\circ_{\text{Ce}^{4+}/\text{Ce}^{3+}} = 1.44$ and $E^\circ_{\text{Fe(phen)}^3+/\text{Fe(phen)}^2+} = 1.06$ [V] (vs. SHE) in 1M H$_2$SO$_4$ medium at 25°C; this fact makes a difference in the reaction pathway between the cerium-catalyzed and the ferroin-catalyzed systems, as mentioned in Section 2. However, a theoretical determination of the standard redox potential for a general mixed solution is not only difficult but also involves indistinguishable chemical elements because of the coexistence of a number of ion equilibria. At the same time, because the color of the solution changes with changing concentration ratios of catalytic ions, the fluctuation of $E_{\text{ORP}} - E^\circ$ is more significant than the level of $E_{\text{ORP}}$.

Systems (T), (RZ), and (CF) represent the cerium-, ferroin-, and cerium–ferroin-catalyzed BZ reactions, respectively. As described in the following sections, each trajectory approaches a closed orbit in the phase space $(x, y, z)$ under an appropriate condition. Figure 3 shows the time sequences of $E_{\text{ORP}} - E^\circ$ corresponding to each closed orbit, that is,

$$E_{\text{ORP}} - E^\circ_T = 0.0261 \ln \frac{Y(t)}{C - Y(t)} \quad \text{for (T)},$$

$$E_{\text{ORP}} - E^\circ_{\text{RZ}} = 0.0261 \ln \frac{Z(t)}{F - Z(t)} \quad \text{for (RZ)}, \quad \text{and}$$

$$E_{\text{ORP}} - E^\circ_{\text{CF}} = 0.0261 \left( \ln \frac{Y(t)}{C - Y(t)} + \ln \frac{Z(t)}{F - Z(t)} \right) \quad \text{for (CF)},$$

where $E^\circ_T$, $E^\circ_{\text{RZ}}$, and $E^\circ_{\text{CF}}$ are the standard redox potentials for each system. Although the detailed values are unavailable, $E^\circ_{\text{RZ}} < E^\circ_{\text{CF}} < E^\circ_T$ is established from a general argument on electrochemistry. As can be seen in Figure 3, the amplitudes for (T), (RZ), and (CF) are respectively 180, 125, and 275 mV, and the periods 74, 37, and 69 s, respectively. The magnitude relation of the oscillation properties agrees with Figure 1. In particular, the waveform of (CF) has the same characteristics as Exp. III. However, this result does not exactly fit the experimental data with
high quantitative accuracy. There are some possible reasons for the discrepancy. One is the difference in rate constant caused by the difference in temperature. Most of the rate constants of Table 3 were estimated at 25°C, whereas the current experiments were carried out at 30°C. The second possible reason is that the values of \(A\) and \(B\) depend on the type of catalyst and the concentration of the \(\text{H}_2\text{SO}_4\) medium.

Obviously, system (1) is more suitable for the simulation than (CF) without the quasi-steady-state approximation if our aim is to reproduce an actual redox curve by means of modeling. There is no need look for quantitative accuracy as far as understanding the mechanism of the color transition.

**Figure 3.** Redox potential curves represented by the solutions of (T), (RZ), and (CF).

Figure 4 illustrates the reason for the six-phase color transition with four colors by employing the periodic solution of (CF). To plot redox potential curve (b) as compared to Exp. III in Figure 1, the level of \(E_{\text{CF}}^0\) is estimated here at

\[
E_{\text{CF}}^0 \approx \left( E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^0 + E_{\text{Fe(phen)}^{3+}/\text{Fe(phen)}^{2+}}^0 \right) / 2 = 1250 \text{ [mV] (vs.SHE)}.
\]

Graph (c) shows the time sequences of \(Y(t)/C\) and \(Z(t)/F\) corresponding to one period of the limit cycle for (CF). It should be noted that \(Y(t)/C\) increases from the minimum to near 1.0 at a slightly earlier moment and at a more rapid rate than \(Z(t)/F\). We assume that at approximately half of these values, the color phases of the cerium ions and the ferroin switch, as shown in gradation (d). At \(t \in (0, 26)\), the cerium ions become colorless in the near-entire trivalent state, whereas the ferroin turns red. As a result, the solution appears red. In the next instant, it turns blue after momentarily turning purple during the oxidation process of ferroin to ferrin. In the subsequent oxidation process of cerous to ceric ions, the solution turns green at \(t = 30\), with the yellow supplied by \(\text{Ce}^{4+}\). The reductions of ceric ions and ferrin begin at \(t = 33\). The solution turns blue, purple, and red, in that order, with decreasing concentrations of \(\text{Ce}^{4+}\) and \(\text{Fe(phen)}^{3+}\). In this way, color sequence (a) is completed. This cycle is repeated with every period of the redox potential curve.

5. **Hopf bifurcation analysis.** This section examines the possibility of a Hopf bifurcation for (CF), particularly in the three cases to set the bifurcation parameter for \(\varepsilon, \xi_1, \) or \(\xi_2\). To state the main results, we need some preliminaries. Write \((\dot{\cdot}) = d/d\tau\).

**Lemma 5.1.** For (CF), the set

\[
\Omega_0 = \{(x, y, z) \in \Omega : \mu < x < 1, 0 < y < 1, 0 < z < 1\}
\]
Figure 4. The rule of color transition for the BZ reaction catalyzed by cerium ions and ferroin: (a) the color sequence of the reaction solution, (b) the redox potential curve generated by (CF), (c) the time sequences of the ratios of Ce\(^{4+}\) and Fe(phen)\(^{3+}\) to the total cerium ion and ferroin concentrations, (d) the color phases exhibited by the cerium ions and ferroin. The solution color changes in six phases of four colors because of the simultaneous continuous fluctuation of the ratios between the oxidant and reductant of each ion.

is positively invariant.

Proof. Let us put

\[
\begin{align*}
\Omega_1 &= \{(x, y, z) \in \Omega : 0 \leq x \leq \mu\}, \\
\Omega_2 &= \{(x, y, z) \in \Omega : x \geq 1\}, \\
\partial_1 &= \{(x, y, z) \in \Omega : \mu \leq x \leq 1, \ y = 0\}, \\
\partial_2 &= \{(x, y, z) \in \Omega : \mu \leq x \leq 1, \ z = 0\},
\end{align*}
\]

and for \(0 < \delta < 1\)

\[
\begin{align*}
\partial_3(\delta) &= \{(x, y, z) \in \Omega : \mu \leq x \leq 1, \ y = 1 - \delta\}, \\
\partial_4(\delta) &= \{(x, y, z) \in \Omega : \mu \leq x \leq 1, \ z = 1 - \delta\}.
\end{align*}
\]

The first equation of (CF) gives \(\dot{x} > 0\) for any point in \(\Omega_1 \setminus \{(0, 0, 0)\}\) and also \(\dot{x} < 0\) for \(\Omega_2 \setminus \{(1, 0, 0)\}\). The second and third equations give

\[
\begin{align*}
\dot{y} &= \frac{\eta x(1 + \beta_2 z)}{\xi_1(1 - z + \eta)} > 0 \quad \text{for } \partial_1 \quad \text{and} \quad \dot{z} = \frac{x(1 + \beta_1 y)}{\xi_2(1 + \eta(1 - y))} > 0 \quad \text{for } \partial_2
\end{align*}
\]

respectively. Moreover,

\[
\xi_1 \dot{y} = \frac{\delta \eta x(1 + \beta_2 z)}{1 - z + \delta \eta} - (1 - \delta) \left\{ \alpha_1 + \frac{\beta_1 x(1 - z)}{1 - z + \delta \eta} \right\} \quad \text{for } \partial_3(\delta),
\]

so that \(\dot{y} \to -(\alpha_1 + \beta_1 x)/\xi_1 < 0\) as \(\delta \to 0\). In the same manner,

\[
\xi_2 \dot{z} = \frac{\delta x(1 + \beta_1 y)}{\delta + \eta(1 - y)} - \alpha_2 \left( \frac{1}{\delta - 1} \right) - (1 - \delta) \frac{\beta_2 \eta x(1 - y)}{\delta + \eta(1 - y)} \quad \text{for } \partial_4(\delta),
\]
and so \( z \to -\infty \) as \( \delta \to 0 \). This completes the proof.

\[ \square \]

**Lemma 5.2.** System (CF) has exactly two equilibria in \( \Omega \); one is the origin \( E_0 = (0, 0, 0) \) and the other, written as \( \tilde{E} = (\tilde{x}, \tilde{y}, \tilde{z}) \), is located in \( \Omega_0 \).

**Proof.** Under condition (2), an equilibrium of (CF) is given by the solution of the following system of equations:

\[
\begin{align*}
(1) & \quad x(1 - x) - \frac{x - \mu}{x + \mu}(\alpha_1 y + \frac{\alpha_2 z}{1 - z}) = 0, \\
(2) & \quad x(1 + \beta_2 z) - x(1 + \beta_1 y + \beta_2 z) = 0, \\
(3) & \quad x(1 + \beta_1 y) - \frac{\alpha_2 z}{1 - z} - x(1 + \beta_1 y + \beta_2 z) = 0.
\end{align*}
\]

It is apparent that \( E_0 \) is the above solution. The proof of Lemma 5.1 implies that \( E_0 \) is unstable independently of \( \varepsilon, \xi_1 \), and \( \xi_2 \) and, in addition, if an equilibrium that belongs to \( \Omega \) exists except for \( E_0 \), then the equilibrium is in \( \Omega_0 \).

Summing (4) and (5) gives

\[
x = \alpha_1 y + \frac{\alpha_2 z}{1 - z}.
\]

Equations (3) and (6) yield

\[
x(x^2 + \mu x - 2\mu) = 0.
\]

Equation (7) has a unique positive root, \( \bar{x} \in (\mu, 1) \), where

\[
\bar{x} = \frac{-\mu + \sqrt{\mu(\mu + 8)}}{2}.
\]

Note that \( \bar{x} - \alpha_1 y > 0 \) for the points \((\bar{x}, y, z) \in \Omega_0 \) satisfying (6). Multiplying (4) by \((\bar{x} - \alpha_1 y + \alpha_2)((1 - z) + \eta(1 - y))\) and substituting \( z = \frac{x - \alpha_1 y}{\bar{x} - \alpha_1 y + \alpha_2} \) derived from (6), we have

\[
\eta(1 - y)(\bar{x} - \alpha_1 y)(\bar{x} - \alpha_1 y + \alpha_2 + \beta_2 \bar{x}) - \alpha_2(\alpha_1 + \beta_1 \bar{x})y = 0.
\]

Denote by \( L(y) \) the left side of (9), which is a cubic function. Then

\[
L(0) > 0, \quad L(\bar{x}/\alpha_1) < 0 \quad \text{and} \quad L(1) < 0.
\]

The derivative of \( L(y) \) is given by

\[
L'(y) = -\eta(\bar{x} - \alpha_1 y + \alpha_1(1 - y))(\bar{x} - \alpha_1 y + \alpha_2 + \beta_2 \bar{x}) - \eta(1 - y)(\bar{x} - \alpha_1 y - \alpha_2)(\alpha_1 + \beta_1 \bar{x}).
\]

It follows that \( L'(y) < 0 \) for any \( y \in [0, \min(1, \bar{x}/\alpha_1)] \). Therefore, a unique zero \( \bar{y} \in (0, 1) \) of \( L(y) \) can attain the equilibrium of (CF).

Finally, we obtain \( \tilde{z} = (\bar{x} - \alpha_1 \bar{y})/(\bar{x} - \alpha_1 \bar{y} + \alpha_2) \in (0, 1) \).

Our most important result is the following theorem for the case in which we take \( \varepsilon \) as the bifurcation parameter.

**Theorem 5.3.** Suppose that

\[
\mu < -\frac{13 + 5\sqrt{7}}{3}.
\]

Then system (CF) has a unique simple Hopf bifurcation point.
Proof. Put \( \sigma = \varepsilon^{-1} \). With the aid of (4), (5), and (6), the Jacobian matrix \( \tilde{J} \) for (CF) at \( \bar{E} \) is written as

\[
\tilde{J} = \tilde{J}(\sigma) = \begin{pmatrix}
\sigma a_{11} & -\sigma a_{12} & -\sigma a_{13} \\
a_{21}/\xi_1 & -a_{22}/\xi_1 & a_{23}/\xi_1 \\
a_{31}/\xi_2 & a_{32}/\xi_2 & -a_{33}/\xi_2
\end{pmatrix},
\]

where

\[
a_{11} = 1 - 2\bar{x} - \frac{2\mu\bar{x}}{(\bar{x} + \mu)^2}, \quad a_{12} = a_1(1 - \bar{x}), \quad a_{13} = \frac{\alpha_2(1 - \bar{x})}{(1 - \bar{z})^2},
\]

\[
a_{21} = \frac{a_1\bar{y}}{\bar{x}}, \quad a_{22} = a_1 + \frac{c_2\bar{x}}{c_0} + \frac{\eta_2\bar{z}}{c_0 1 - \bar{z}}, \quad a_{23} = \frac{c_1\bar{x}}{c_0} + \frac{a_1\bar{y}}{c_0},
\]

\[
a_{31} = \frac{a_2\bar{z}}{\bar{x}(1 - \bar{z})}, \quad a_{32} = \frac{c_2\bar{x}}{c_0} + \frac{\eta_2\bar{z}}{c_0 1 - \bar{z}}, \quad a_{33} = \frac{\alpha_2}{(1 - \bar{z})^2} + \frac{c_1\bar{x}}{c_0} + \frac{a_1\bar{y}}{c_0},
\]

\( c_0 = (1 - \bar{z}) + \eta(1 - \bar{y}), \quad c_1 = \beta_1\bar{y} + \eta\beta_2(1 - \bar{y}), \quad c_2 = \beta_1(1 - \bar{z}) + \eta\beta_2\bar{z}. \)

Clearly, \( a_{12}, a_{13}, a_{21}, a_{22}, a_{23}, a_{31}, a_{32}, \) and \( a_{33} \) are positive.

Condition (10) is transformed into

\[
\mu < \frac{4(3 - \sqrt{7})^2}{8 - 4(3 - \sqrt{7})}.
\]

Moreover

\[
\mu(\mu + 8) < \left( \mu + 2(3 - \sqrt{7}) \right)^2,
\]

thus

\[
-\mu + \sqrt{\mu(\mu + 8)} < 2(3 - \sqrt{7}). \tag{11}
\]

Using \( \mu = \bar{x}^2/(2 - \bar{x}) \) of (7), (8), and (11) with \( \bar{x} < 1 \), we obtain

\[
a_{11} = \bar{x}^2 - 6\bar{x} + 2 = \frac{\bar{x} - 3 - \sqrt{7}}{4} \left( -\mu + \sqrt{\mu(\mu + 8)} - 2(3 - \sqrt{7}) \right) > 0.
\]

Define the characteristic polynomial \( p(\lambda; \sigma) \) of \( \tilde{J} \) by

\[
p(\lambda; \sigma) = \det (\lambda I - \tilde{J}) = \lambda^3 + p_1(\sigma)\lambda^2 + p_2(\sigma)\lambda + p_3(\sigma), \tag{12}
\]

where the coefficients are affine functions as follows:

\[
p_1(\sigma) = -\sigma a_{11} + \left( \frac{a_{22}}{\xi_1} + \frac{a_{33}}{\xi_2} \right),
\]

\[
p_2(\sigma) = \sigma \left( \frac{a_{12}a_{21}}{\xi_1} + \frac{a_{13}a_{31}}{\xi_2} - a_{11} \left( \frac{a_{22}}{\xi_1} + \frac{a_{33}}{\xi_2} \right) + \frac{a_{22}a_{33} - a_{23}a_{32}}{\xi_1\xi_2} \right),
\]

\[
p_3(\sigma) = \sigma \left( \frac{a_{12}(a_{23}a_{31} + a_{21}a_{33}) + a_{13}(a_{21}a_{32} + a_{22}a_{31}) - a_{11}(a_{22}a_{33} - a_{23}a_{32})}{\xi_1\xi_2} \right).
\]

Letting \((\ )' = d/d\sigma\), the above functions are rewritten in the forms

\[
p_1(\sigma) = p_1'(\sigma) + p_{10}, \quad p_2(\sigma) = p_2'(\sigma) + p_{20}, \quad p_3(\sigma) = p_3'(\sigma).
\]

It is obvious that \( p_1' < 0 \) and \( p_{10} > 0 \). Putting the zero of \( p_1(\sigma) \)

\[
\sigma_1 = \frac{a_{22}/\xi_1 + a_{33}/\xi_2}{a_{11}},
\]

we have

\[
p_1(\sigma) > 0 \text{ for } \sigma \in (0, \sigma_1) \quad \text{and} \quad p_1(\sigma) < 0 \text{ for } \sigma > \sigma_1.
\]
Direct computation shows
\[
a_{22}a_{33} - a_{23}a_{32} = \frac{\alpha_1}{c_0} (c_1 \bar{x} + \alpha_1 \bar{y}) + \frac{\alpha_2}{(1 - \bar{z})^2} \left( \alpha_1 + \frac{c_2 \bar{x}}{c_0} + \frac{\eta}{c_0} \frac{\alpha_2 \bar{z}}{1 - \bar{z}} \right), \tag{13}
\]
\[
a_{12}(a_{23}a_{31} + a_{21}a_{32}) = \alpha_1 (1 - \bar{x}) \left( \frac{1}{c_0} (c_1 \bar{x} + \alpha_1 \bar{y}) + \frac{\alpha_1 \alpha_2 \bar{y}}{\bar{x}(1 - \bar{z})^2} \right), \tag{14}
\]
\[
a_{13}(a_{21}a_{32} + a_{22}a_{31}) = \frac{\alpha_2 (1 - \bar{x})}{(1 - \bar{z})^2} \left( \frac{c_2 \bar{x}}{c_0} + \frac{\eta}{c_0} \frac{\alpha_2 \bar{z}}{1 - \bar{z}} + \frac{\alpha_1 \alpha_2}{\bar{x}(1 - \bar{z})} \right). \tag{15}
\]
Relation (13) means \( p_{20} > 0 \). Employing (13), (14), and (15), we find
\[
p_3 = \frac{1 - \bar{x} - a_{11}}{\xi_1 \xi_2} \left( \frac{\alpha_1}{c_0} (c_1 \bar{x} + \alpha_1 \bar{y}) + \frac{c_2 \alpha_2 \bar{x}}{c_0 (1 - \bar{z})^2} + \frac{\eta}{c_0} \frac{\alpha_2 \bar{z}}{1 - \bar{z}} + \frac{\alpha_1 \alpha_2}{(1 - \bar{z})^2} \right) > 0,
\]
which leads to
\[
p_3(\sigma) > 0 \text{ for any } \sigma > 0.
\]
The Hurwitz matrix \( \mathcal{H}_p(\sigma) \) for (12) is given by the form
\[
\mathcal{H}_p(\sigma) = \begin{pmatrix} p_1(\sigma) & p_3(\sigma) & 0 \\ 1 & p_2(\sigma) & 0 \\ 0 & p_1(\sigma) & p_3(\sigma) \end{pmatrix}. \tag{16}
\]
In addition, the first- and second-order Hurwitz determinants are respectively
\[
\Delta_1(\sigma) = p_1(\sigma) \quad \text{and} \quad \Delta_2(\sigma) = p_1(\sigma)p_2(\sigma) - p_3(\sigma).
\]
One can immediately see that
\[
\Delta_2(0) = p_{10}p_{20} > 0 \quad \text{and} \quad \Delta_2(\sigma_1) = -p_3(\sigma_1) < 0. \tag{17}
\]
The remaining argument is divided into the three cases of (i) \( p'_2 > 0 \), (ii) \( p'_2 < 0 \), and (iii) \( p'_2 = 0 \).

(i) If \( p'_2 > 0 \), then \( p_2(\sigma) > 0 \) for any \( \sigma > 0 \). Quadratic function \( \Delta_2(\sigma) \) is concave because \( \Delta'_2 = 2p'_1p'_2 < 0 \). Employing (17), there exists uniquely \( \sigma^* \in (0, \sigma_1) \) such that
\[
p_3(\sigma^*) > 0, \quad \Delta_1(\sigma^*) > 0, \quad \Delta_2(\sigma^*) = 0 \quad \text{and} \quad \Delta'_2(\sigma^*) < 0. \tag{18}
\]
To be precise,
\[
\sigma^* = \frac{p'_3 - p'_1p_{20} - p'_2p_{10} + \sqrt{(p'_3 - p'_1p_{20} - p'_2p_{10})^2 - 4p'_1p'_2p_{10}p_{20}}}{2p'_1p'_2}.
\]

(ii) If \( p'_2 < 0 \), then there exists the zero \( \sigma_2 > 0 \) of \( p_2(\sigma) \). Noting that \( \Delta_2(\sigma) \) is convex and \( \Delta_2(\sigma_2) = -p_3(\sigma_2) < 0 \), there exists uniquely \( \sigma^* \in [0, \min(\sigma_1, \sigma_2)] \), satisfying the condition stated in (18); however,
\[
\sigma^* = \frac{p'_3 - p'_1p_{20} - p'_2p_{10} - \sqrt{(p'_3 - p'_1p_{20} - p'_2p_{10})^2 - 4p'_1p'_2p_{10}p_{20}}}{2p'_1p'_2}.
\]

(iii) If \( p'_2 = 0 \), then \( \Delta_2(\sigma) \) is an affine function with \( \Delta'_2 = p'_1p_{20} - p'_3 < 0 \). In this case, \( \sigma^* \in (0, \sigma_1) \) satisfying (18) is uniquely given by
\[
\sigma^* = \frac{p_{10}p_{20}}{p'_3 - p'_1p_{20}}.
\]
Combining (i), (ii), and (iii), we conclude from Theorem A.1 that system (CF) has a unique simple Hopf bifurcation point. That is to say, the stability of \( \bar{E} \) is switched at \( \varepsilon^* = 1/\sigma^* \), and a limit cycle appears for \( \varepsilon < \varepsilon^* \). \( \square \)
We next treat the cases to take $\xi_1$ or $\xi_2$ as the bifurcation parameter. In the case in which the bifurcation parameter is $\xi_1$, we put $\kappa = \xi_1^{-1}$ and $(\gamma)' = d/d\kappa$. The Jacobian matrix $J$ is redefined as a function of $\kappa$, and its characteristic polynomial is given in the form

$$q(\lambda; \kappa) = \lambda^3 + q_1(\kappa)\lambda^2 + q_2(\kappa)\lambda + q_3(\kappa).$$

The coefficients $q_1(\kappa)$, $q_2(\kappa)$, and $q_3(\kappa)$ are affine functions as follows:

$$q_1(\kappa) = a_{22}\kappa + \left(-\frac{a_{11}}{\varepsilon} + \frac{a_{33}}{\xi_2}\right),$$

$$q_2(\kappa) = \kappa \left(\frac{a_{12}a_{21} - a_{11}a_{22}}{\varepsilon} + \frac{a_{22}a_{33} - a_{23}a_{32}}{\xi_2}\right) + \frac{a_{13}a_{31} - a_{11}a_{33}}{\varepsilon\xi_2},$$

$$q_3(\kappa) = \kappa \left(a_{12}(a_{23}a_{31} + a_{21}a_{33}) + a_{13}(a_{21}a_{32} + a_{22}a_{31}) - a_{11}(a_{22}a_{33} - a_{23}a_{32})\right) \varepsilon\xi_2.$$

Meanwhile, in the case where the bifurcation parameter is $\xi_2$, by putting $\kappa = \xi_2^{-1}$, the coefficients of $q(\lambda; \kappa)$ are given as

$$q_1(\kappa) = a_{33}\kappa + \left(-\frac{a_{11}}{\varepsilon} + \frac{a_{22}}{\xi_1}\right),$$

$$q_2(\kappa) = \kappa \left(\frac{a_{13}a_{31} - a_{11}a_{33}}{\varepsilon} + \frac{a_{22}a_{33} - a_{23}a_{32}}{\xi_1}\right) + \frac{a_{12}a_{21} - a_{11}a_{22}}{\varepsilon\xi_1},$$

$$q_3(\kappa) = \kappa \left(a_{12}(a_{23}a_{31} + a_{21}a_{33}) + a_{13}(a_{21}a_{32} + a_{22}a_{31}) - a_{11}(a_{22}a_{33} - a_{23}a_{32})\right) \varepsilon\xi_1.$$

Let us set $q_1(\kappa) = q_1^0 + q_{10}$, $q_2(\kappa) = q_2^0 + q_{20}$, and $q_3(\kappa) = q_3^0 + q_{30}$. It is verified in the proof of Theorem 5.3 that

$$q_1' > 0 \quad \text{and} \quad q_3' > 0.$$

Define the Hurwitz matrix $H(\kappa)$ instead of (16). Then, the second-order Hurwitz determinant can be written as $\Delta_2(\kappa) = q_1(\kappa)q_2(\kappa) - q_3(\kappa)$. Examining the property of $\Delta_2(\kappa)$, we obtain the following theorem. To avoid repeating arguments similar to those given in Theorem 5.3, the proof is omitted here.

**Theorem 5.4.** Suppose that condition (10) holds. The number of simple Hopf bifurcation points for (CF) and the local stability of $\bar{E}$ are sorted by the signs of $q_2$, $q_{10}$, and $q_{20}$ into ten types, as shown in Table 4.

1. **T0** There is no bifurcation point; $\bar{E}$ is unstable for all $\kappa > 0$.
2. **T1** If $q_3^0 - q_1^0q_{20} - q_2^0q_{10} > 4q_1^0q_2^0q_{10}q_{20}$, then two bifurcation points, $\kappa^*_-$ and $\kappa^*_+$, exist; $\bar{E}$ is unstable for $\kappa \in (\kappa^*_-, \kappa^*_+)$. If not, there is no bifurcation point; $\bar{E}$ is stable for all $\kappa > 0$.
3. **T2** If $q_3^0 - q_1^0q_{20} - q_2^0q_{10} > 4q_1^0q_2^0q_{10}q_{20}$, then two bifurcation points, $\kappa^*_-$ and $\kappa^*_+$, exist; $\bar{E}$ is unstable for $\kappa \notin (\kappa^*_-, \kappa^*_+)$. If not, there is no bifurcation point; $\bar{E}$ is unstable for all $\kappa > 0$.
4. **T3** The unique bifurcation point is $\kappa^*_+; \bar{E}$ is unstable for $\kappa < \kappa^*_+$.
5. **T4** The unique bifurcation point is $\kappa^*_+; \bar{E}$ is unstable for $\kappa > \kappa^*_+$.
6. **T5** If $q_2^0q_{10} < q_3^0$, then the unique bifurcation point is $\kappa^*_+; \bar{E}$ is unstable for $\kappa < \kappa^*_+$. If not, there is no bifurcation point; $\bar{E}$ is stable for all $\kappa > 0$.
7. **T6** If $q_1^0q_{20} < q_3^0$, then the unique bifurcation point is $\kappa^*_+; \bar{E}$ is unstable for $\kappa < \kappa^*_+$. If not, there is no bifurcation point; $\bar{E}$ is stable for all $\kappa > 0$. 
T7) If \( q'_1 q_{20} < q'_3 \), then the unique bifurcation point is \( \kappa_0^* \); \( \bar{E} \) is unstable for \( \kappa > \kappa_0^* \). If not, there is no bifurcation point; \( \bar{E} \) is stable for all \( \kappa > 0 \).

T8) If \( q'_1 q_{20} > q'_3 \), then the unique bifurcation point is \( \kappa_0^* \); \( \bar{E} \) is unstable for \( \kappa < \kappa_0^* \). If not, there is no bifurcation point; \( \bar{E} \) is unstable for all \( \kappa > 0 \).

T9) There is no bifurcation point. If \( q'_1 q_{20} > q'_3 \), then \( \bar{E} \) is stable for all \( \kappa > 0 \). If not, \( \bar{E} \) is unstable for all \( \kappa > 0 \).

Here

\[
\kappa_0^* = \frac{q_{10} q_{20}}{q'_3 - q'_1 q_{20}}.
\]

and

\[
\kappa_0^* = \frac{q_{10} q_{20}}{q'_3 - q'_1 q_{20}}.
\]

Table 4. Relation between signs of \( q'_2 \), \( q_{10} \), \( q_{20} \), and bifurcation type.

| \( q'_2 \) | \( q_{10} \) | \( q_{20} \) | type | \( q'_2 \) | \( q_{10} \) | \( q_{20} \) | type |
|---|---|---|---|---|---|---|---|
| + | + | + | T1 | 0 | + | + | T7 |
| + | + | 0 | T5 | 0 | + | 0 | T0 |
| + | + | - | T3 | 0 | + | - | T0 |
| + | 0 | + | T6 | 0 | 0 | + | T9 |
| + | 0 | 0 | T3 | 0 | 0 | 0 | T0 |
| + | 0 | - | T3 | 0 | 0 | - | T0 |
| + | - | + | T3 | 0 | - | + | T8 |
| + | - | 0 | T3 | 0 | - | 0 | T0 |
| + | - | - | T3 | 0 | - | - | T0 |

6. Bifurcation diagram. This section is devoted to demonstrating our result for model (CF) with numerical examples. Based on Table 3, the parameter values are set as follows:

\[
\varepsilon = 7.58824 \times 10^{-3}, \quad \xi_1 = 0.1517, \quad \xi_2 = 3.25 \times 10^{-3},
\]

\[
\mu = 3.95349 \times 10^{-4}, \quad \eta = 0.500123,
\]

\[
\alpha_1 = 0.321796, \quad \alpha_2 = 9.89897 \times 10^{-4}, \quad \beta_1 = 5.43314, \quad \beta_2 = 0.0125969.
\]

As a result

\[
\bar{E} = (0.0279224, 0.06391, 0.881397).
\]

As seen from the above and noting that \(-131.5x^2 \approx 0.0762522\), condition (10) holds.

The first example shown in Figure 5 was performed by varying \( \sigma \) \((= \varepsilon^{-1})\) instead of varying \( \varepsilon \). Now, \( p'_2 = -29.5534 \), which corresponds to case (ii) in the proof of Theorem 5.3. In fact, \( \sigma_1 = 43.5155, \sigma_2 = 2.77303 \), and the Hopf bifurcation point \( \sigma^* = 2.76166 \). Because an easy simulation near the bifurcation point indicates the existence of a limit cycle with a small amplitude for some \( \sigma < \sigma^* \), e.g. \( \sigma = 2.740 \), the Hopf bifurcation caused by this parameter set is expected to be the subcritical type, however, its theoretical proof is beyond the aim of the current paper.

Figure 6 illustrates an example of varying \( \kappa \) \((= \xi_1^{-1})\). In this case, we have \( q'_1 = 0.358995, q_{10} = -83.1873, q'_2 = -0.0948147, q_{20} = -3812.08, \) and \( q'_3 = 94.3284 \), and therefore system (CF) shows the dynamics of the T0-type stated in Theorem 5.4.

Figure 7 gives an example of varying \( \kappa \) \((= \xi_2^{-1})\). In this situation, \( q'_1 = 0.122226, q_{10} = -118.516, q'_2 = -12.1229, q_{20} = -82.5546, \) and \( q'_3 = 1.94646 \), and as a
Figure 5. Bifurcation diagram obtained by varying $\varepsilon$: (a) The state-space plot of the $\omega$-limit sets by setting $\sigma = 3.0$ and 20.0 every 1.0; the orbits of (CF) approach the equilibrium $\bar{E}$ for every $\sigma < \sigma^*$, whereas a limit cycle appears around $\bar{E}$ for each $\sigma > \sigma^*$. (b) The time sequence $y(\tau)$, $z(\tau)$ of the solution for the initial condition $(x_0, y_0, z_0) = (0.5, 0.1, 0.3)$ at $\sigma = 2.7, 2.8, 5.0, 10.0$. An increase in $\sigma$ enlarges the frequency and the amplitude of oscillation.

result, the dynamics come to the same type as that of the last example. In both figures, each $\omega$-limit set forms a closed orbit in $\Omega_0$, but a bifurcation phenomenon of $\bar{E}$ cannot be observed. The parameter set of Table 3 does not generate a Hopf bifurcation with respect to $\xi_1$ and $\xi_2$. Considering from a different perspective, this means that a bifurcation point does not exist for any $\xi_1$ or any $\xi_2$. These results also coincide with the fact that the redox potential oscillates even in the absence of either ferroin or cerium ions.

It is apparent that $\varepsilon$, $\xi_1$, and $\xi_2$ each have a role in the time constant for (CF), so that the bifurcation parameter of the present analysis has a direct effect on the frequency or period of oscillation through numerical simulation. Generally speaking, smaller time constants, namely, larger values of $\sigma$ and $\kappa$, provide more rapid responses to the system.

7. Concluding remarks. The color transition of the BZ reaction system catalyzed by cerium ions and ferroin is a well-recognized phenomenon from the experimental aspect. This paper presents a three-variable model (CF) by interlacing the RZ model and the Tyson model to theoretically describe the six-phase color transition of four colors. In particular, we not only established a Hopf bifurcation theorem with a simple condition for the value of $\mu$ by using Liu’s method, but also gave the bifurcation point $\sigma^*$ with an exact formula.

Real oscillations of the BZ reaction systems catalyzed by multiple ion types sometimes exhibit chaotic behavior. However, the model (CF) has no chaotic orbits because the system itself is composed of a homotopy between the RZ model and the Tyson model, both of which never show chaotic behavior. This indicates the limitation of (CF) as a model. It should also be emphasized that widely varying
Figure 6. $\omega$-limit sets obtained by varying $\xi_1$: (a) The phase-space plots for $\kappa (= \xi_1^{-1})$ between 0.1 and 10.1 every 0.5; the equilibrium $\bar{E}$ is always unstable. (b) The time-sequence $y(\tau), z(\tau)$ of the solution for the initial condition $(x_0, y_0, z_0) = (0.5, 0.1, 0.3)$ at $\kappa = 0.1, 0.3, 1.0, 10.0$; the period of the limit cycle is almost proportional to $\kappa$ as long as $\kappa$ is small.

Figure 7. $\omega$-limit sets obtained by varying $\xi_2$: (a) The phase-space plots for $\kappa (= \xi_2^{-1})$ between 0.1 and 50.1 every 2.5; the equilibrium $\bar{E}$ is always unstable. (b) The time-sequence $y(\tau), z(\tau)$ of the solution for the initial condition $(x_0, y_0, z_0) = (0.5, 0.1, 0.3)$ at $\kappa = 0.1, 3.0, 10.0, 50.0$; the period of limit cycle is almost proportional to $\kappa$ as long as $\kappa$ is small.

the specified bifurcation parameter is impractical for real reaction systems because of the loss of hypothesis at fixed concentrations and rate constants.

One of the remaining problems conceived immediately is to analyze the cases of general $r$ and $q$. When these are answered, (CF) will extend the describable
Appendix. This section introduces a Hopf bifurcation theorem established by Liu [11] without the proof. In [1], the author developed the techniques to apply Liu’s theorem to a higher-order system with a rigorous computation through the bifurcation analysis for CTL dynamics.

Consider a system of differential equations with a single parameter

\[ \dot{x} = f_\mu(x), \quad x \in \mathbb{R}^n, \quad \mu \in \mathbb{R}, \tag{19} \]

where \( f_\mu \) is smooth for every \( \mu \). Assume that (19) has an equilibrium \((x_0, \mu_0)\), that is, \( f_{\mu_0}(x_0) = 0 \). Let \( D_x f_\mu(x) \) be the Jacobian matrix of \( f_\mu \). Define the characteristic polynomial of \( D_x f_\mu(x) \) by

\[ p(\lambda; \mu) = a_0(\mu) \lambda^n + a_1(\mu) \lambda^{n-1} + \cdots + a_n(\mu), \quad a_0(\mu) > 0, \tag{20} \]

where \( a_0, a_1, \ldots, a_n \) are smooth functions of \( \mu \). Then, the Hurwitz matrix \( \mathcal{H}_p(\mu) \) for (20) is given by the square matrix of order \( n \)

\[
\mathcal{H}_p(\mu) = \begin{pmatrix}
a_1(\mu) & a_3(\mu) & a_5(\mu) & a_7(\mu) & \cdots \\
a_0(\mu) & a_2(\mu) & a_4(\mu) & a_6(\mu) & \cdots \\
0 & a_1(\mu) & a_3(\mu) & a_5(\mu) & \cdots \\
0 & a_0(\mu) & a_2(\mu) & a_4(\mu) & \cdots \\
\vdots & \vdots & \vdots & \vdots & \ddots
\end{pmatrix},
\]

where \( a_i(\mu) \equiv 0 \) for \( i > n \). Let us denote by \( \Delta_i(\mu) \) the \( i \)th leading principal minor of \( \mathcal{H}_p(\mu) \), which is called the Hurwitz determinant of order \( i \).

**Theorem A.1 (Liu [11]).** Suppose that there is a smooth curve of equilibria \((x(\mu), \mu)\) with \( x(\mu_0) = x_0 \) for (19), and the following conditions hold:

\begin{enumerate}
\item[(L1)] \( a_n(\mu_0) > 0, \Delta_1(\mu_0) > 0, \ldots, \Delta_{n-2}(\mu_0) > 0, \Delta_{n-1}(\mu_0) = 0; \)
\item[(L2)] \( \frac{d}{d\mu} \Delta_{n-1}(\mu_0) \neq 0. \)
\end{enumerate}

Then, a simple Hopf bifurcation occurs at \( \mu = \mu_0 \).

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