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Numerical analysis on the complex dynamics in a chemical system

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In this paper we present numerical analysis on the complex dynamics in the bromate-MA-ferroin chemical system. A rigorous computer-assisted proof for the existence of limit cycle of the system is presented by means of the Fixed-point theorem for some parameters. By virtue of a recent result of horseshoes theory in dynamical systems, we give a rigorous computer-assisted proof for chaotic behaviors of the attractors of the system for another range of parameters. A quantitative description of the complexity of the bromate-MA-ferroin system is given through topological entropy.

KEY WORDS: Horseshoe, poincaré map, attractor, entropy, bifurcation, limit cycle, the bromate-MA-ferroin system

1. Introduction

Mixed-mode oscillations and deterministic chaos are observed in various nonlinear chemical reactions [1–9]. In particular, such modes have been observed in the Belousov–Zhabotinskii (BZ) reaction [1,2,4–7], halogen [1,2] and oxygen oscillators [8], heterogeneous catalytic [1–3] and electrochemical reactions [9,10]. Various chemical schemes have been proposed to describe experimentally observed self-oscillating modes and their bifurcations [1–3,5–8]. Most of these schemes describe transformations of a rather large number of chemical compounds, which dictates a numerical solution of the corresponding systems of kinetic equations with high dimensionality (3 or more).

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The BZ reaction (oxidation of organic reagents by bromate, catalyzed by metal ions) is the best-known chemical system in which various concentration oscillations have been observed. "Transient period adding" has been observed in the BZ reaction catalyzed by ferroin if initial malonic acid (MA) concentration was varied. Experimental results showing regular transient behaviors in a bromate-MA-ferroin system are described in [11]. The influence of initial ferroin concentration on the regularities in the transient regime has been studied in [11].

In this paper we present numerical analysis on the complex dynamics in the bromate-MA-ferroin chemical system. Limit cycles are studied for some parameters by a rigorous computer-assisted proof; chaotic behaviors of the attractors of the system is studied for some parameters by virtue of a recent result of horseshoes theory in dynamical systems [12,13]. Finally, we give an approximate quantitative estimation of the dynamical complex of the system in terms of topological entropy [14].

2. A model of the bromate-MA-ferroin system

We study the chaotic property of the bromate-MA-ferroin system by analyzing the following system of equations:

$$\begin{aligned} \dot{x} &= \alpha(y - x^3 + \mu_1 x) \\ \dot{y} &= \mu_2 x - y + z + q \\ \dot{z} &= \gamma(x - z), \end{aligned} \tag{1}$$

where $\alpha, \gamma, \mu_1, \mu_2$ and q are guiding parameters.

In [11], an approach has been proposed for finding the conditions for the existence of mixed-mode oscillations and deterministic chaos in a kinetic scheme (1) after reduction to system (1), in which mixed-mode oscillations (MMO) and deterministic chaos are observed [11]. Deterministic chaos is considered to arise as the result of bifurcations of the mixed-mode oscillations [11].

3. Bifurcations

Figure 1(a) and (b) are the bifurcation plots of (1) as we adjust q and fix the initial condition $(0.1820, -0.0946, 0.2507)$; Figure 1(c) and (d) are the peak-bifurcation plots of (1) which are drawn based on the theory of peak to peak [15] (The theory of peak to peak is devoted to the study of a particular form of deterministic chaos).

It can be seen from figure 1, for some value of q, there is only one $x(z)$ corresponding to it. This shows that a periodic orbit exists for certain q, for example $q = 0.01$ and $q = 0.015$.

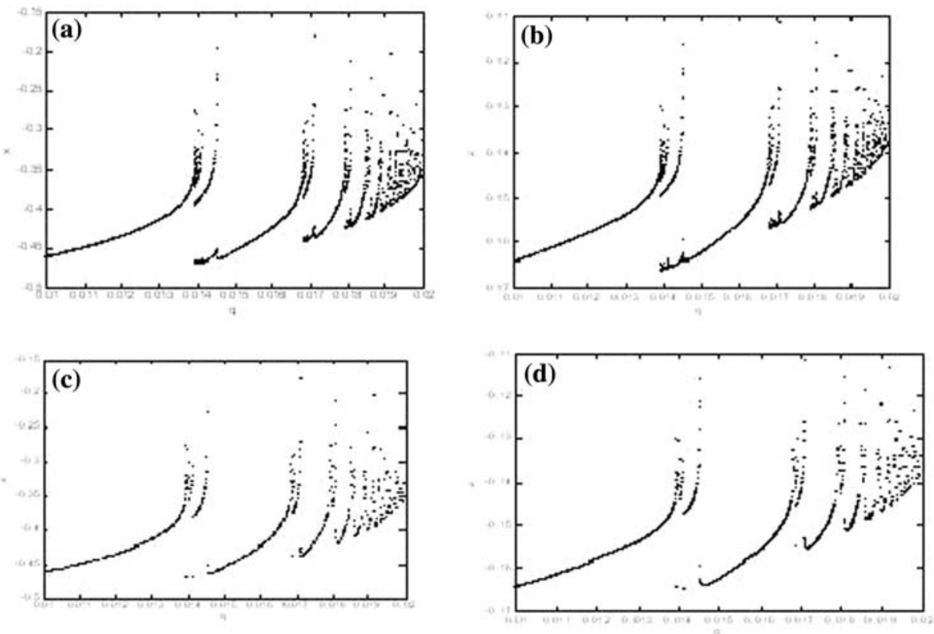

Figure 1. The bifurcation plot of (1) as we adjust q; (a) The bifurcation plot of (1) with the respects to x; (b) The bifurcation plot of (1) with the respects to z; (c) The peak-bifurcation plot of (1) with the respects to x; (d) The peak-bifurcation plot of (1) with the respects to z.

4. Limit cycle and fixed-point theorem

In order to discuss limit cycle, we recall the Fixed-point theorem.

Fixed-point theorem: If $G \subset R^n$ is a bounded closed set homeomorphic to ball, $F: G \to G$ is continuous map, and $F(G) \subset G$, then a fixed point exists in G.

In (1), let $\alpha = 18.7$, $\gamma = 4.35$, $\mu_1 = 0.44$, $\mu_2 = -1.43$, $q = 0.01$, we have phase portraits of (1) as shown in figure 2. Denote by $\varphi(x, t)$ the solution of (1) with initial condition x, i.e. $\varphi(x, 0) = x$. Consider the cross-section M_1 as shown in figure 2, with its four vertexes being $(-0.6, 0.1, -0.25)$, $(-0.4, 0.1, -0.25)$, $(-0.4, 0.1, -0.34)$ and $(-0.6, 0.1, -0.34)$.

We will study the corresponding map on a subset of M_1 as shown in figure 2(a). We select the quadrangle $|ABCD|_1$ with its vertexes being $(-0.5086, 0.1, -0.3021)$, $(-0.5060, 0.1, -0.3023)$, $(-0.5061, 0.1, -0.3040)$ and $(-0.5089, 0.1, -0.3038)$.

$$F: |ABCD|_1 \to M_1.$$

The map F is defined as follows: for each point $x \in |ABCD|_1$, $F(\mathrm{x})$ is the first return intersection point with M_1 under the flow with initial condition x. It can be seen from computer simulation that $F(|ABCD|_1) \subset |ABCD|_1$ as described

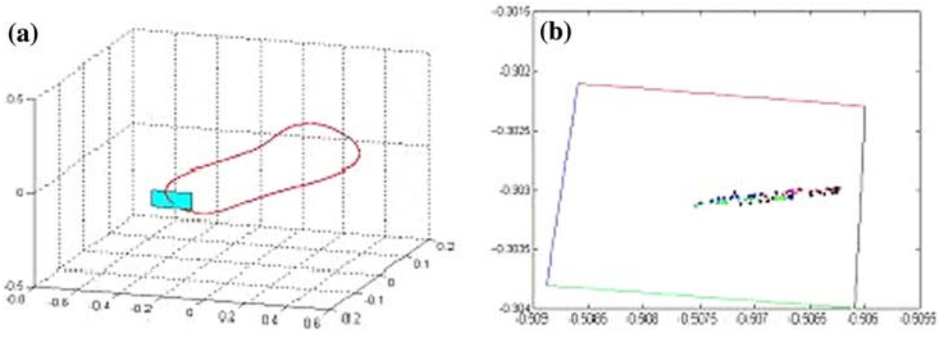

Figure 2. (a) The cross-section M_1 and a limit cycle; (b) The quadrangle $|ABCD|_1$ and its image under map F.

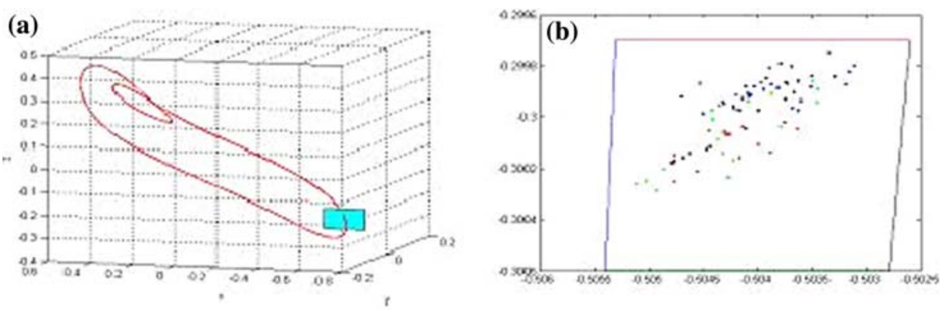

Figure 3. (a) The cross-section M_1 and a limit cycle; (b) The quadrangle $|ABCD|_2$ and its image under map F.

in figure 2(b). According to the Fixed-point theorem, there exists a fixed point, which shows that system (1) has a periodic orbit when $q = 0.01$, and figure 2(a) shows that the periodic orbit is a limit cycle.

When $\alpha = 18.7$, $\gamma = 4.35$, $\mu_1 = 0.44$, $\mu_2 = -1.43$, $q = 0.015$, we have phase portraits of equation (1) as shown in figure 3. Consider the same cross-section M_1.

Select the quadrangle $|ABCD|_2$ with its vertexes being $(-0.5053, 0.1, -0.2997)$, $(-0.5026, 0.1, -0.2997)$, $(-0.5028, 0.1, -0.3006)$ and $(-0.5054, 0.1, -0.3006)$.

$$F : |ABCD|_2 \to M_1.$$

It can be seen form numerical experiment that $F(|ABCD|_2) \subset |ABCD|_2$ as described in figure 3(b). According to the Fixed-point theorem, there exists a fixed point, which shows that system (1) has a periodic orbit when $q = 0.015$, and figure 3(a) shows that the periodic orbit is a limit cycle.

In fact, a limit cycle exists in the system when q varies between 0.01 and 0.015. It can be verified by Fixed-point theorem.

5. Review of a topological Horseshoe theorem

In this section, we recall a result on horseshoes theory developed in [12], which is essential for rigorous verification of existence of chaos in the bromate-MA-ferroin system discussed in this paper.

Let X be a metric space, D is a compact subset of X, and $f\colon D \to X$ is map satisfying the assumption that there exist m mutually disjoint compact subsets $D_1, \dots, D_m$ of D, the restriction of f to each D_i i.e., $f|D_i$ is continuous.

Definition 1. Let γ be a compact subset of D, such that for each $1 \leqslant i \leqslant m$, $\gamma_i = \gamma \cap D_i$ is nonempty and compact, then γ is called a connection with respect to $D_1, \dots, D_m$.

Let F be a family of connections γs with respect to $D_1, \dots, D_m$ satisfying the following property:

$$\gamma \in F \Rightarrow f(\gamma_i) \in F.$$

Then F is said to be a f-connected family with respect to $D_1, \dots, D_m$.

Theorem 2. Suppose that there exists a f-connected family F with respect to disjointed compact subsets $D_1, \dots, D_m$. Then there exists a compact invariant set $K \subset D$, such that $f|K$ is semi-conjugate to m-shift

For the proof of this theorem, see [12].

Here the "semi-conjugate to the m-shift" is conventionally defined in the following sense. If there exists a continuous and onto map

$$h\colon K \to \sum\nolimits_m,$$

such that $h \circ f = \sigma \circ h$, then f is said to be semi-conjugate to σ, where σ is the m-shift (map) and $\sum_m$ is the space of symbolic sequences to be defined below. Let $S_m = \{1, \dots, m\}$ be the set of nonnegative successive integer from 1 to m. Let $\sum_m$ be the collection of all one-infinite sequences with their elements of S_m, i.e., every element s of $\sum_m$ is of the following form:

$$s = \{s_1, \dots, s_m, \dots\}, \quad s_i \in S_m.$$

Now consider another sequence $\bar{s}_i \in S_m$. The distance between s and $\bar{s}$ is defined as

$$d(s, \bar{s}) = \sum_{i=1}^{+\infty} \frac{1}{2^{|i|}} \frac{|s_i - \bar{s}_i|}{|s_i - \bar{s}_i| + 1} \tag{2}$$

with the distance defined as (2), $\sum_m$ is a metric space, and the following facts are well known [16].

For the concept of topological entropy, the reader can refer to [17]. We just recall the result stated in the Lemma 3, which will be used in this paper.

Lemma 3. Let X be a compact metric space, and $f{:}X \to X$ a continuous map. If there exists an invariant set $\Lambda \subset X$ such that $f|\Lambda$ is semi-conjugate to the m-shift σ, then

$$h(f) \geqslant h(\sigma) = \log m,$$

where $h(f)$ denotes the entropy of the map f. In addition, for every positive integer k,

$$h(f^k) = kh(f).$$

6. Symmetries of the system

Fix parameter α, γ, μ_1, μ_2, $\alpha = 18.7$, $\gamma = 4.35$, $\mu_1 = 0.44$, $\mu_2 = -1.43$, let q vary in a certain range. Then an interesting phenomenon appears: There exists some symmetry with respect to state variables and parameter q in the system as shown in figure 4.

By the transform:

$$\begin{aligned} \bar{x} &= -x \\ \bar{y} &= -y \\ \bar{z} &= -z \\ \bar{q} &= -q \end{aligned} \tag{3}$$

we get the equivalent system from (1) as follows:

$$\begin{aligned} \dot{\bar{x}} &= \alpha(\bar{y} - \bar{x}^3 + \mu_1 \bar{x}) \\ \dot{\bar{y}} &= \mu_2 \bar{x} - \bar{y} + \bar{z} + \bar{q} \\ \dot{\bar{z}} &= \gamma(\bar{x} - \bar{z}). \end{aligned} \tag{4}$$

It follows that the system (1) is symmetry about $x = 0$, $y = 0$, $z = 0$, $p = 0$.

Figure 5 is the three Lyapunov exponents of system (1) when q varies between -0.1 and 0.1. It can be seen from figure 5 that the three Lyapunov exponents is approximately symmetry about $q = 0$. The Lyapunov exponent algorithm used here was proposed in [18].

A limit cycle seems exist when $q = 0.0186$ according to computed Lyapunov exponents, and we have the same result by means of other different

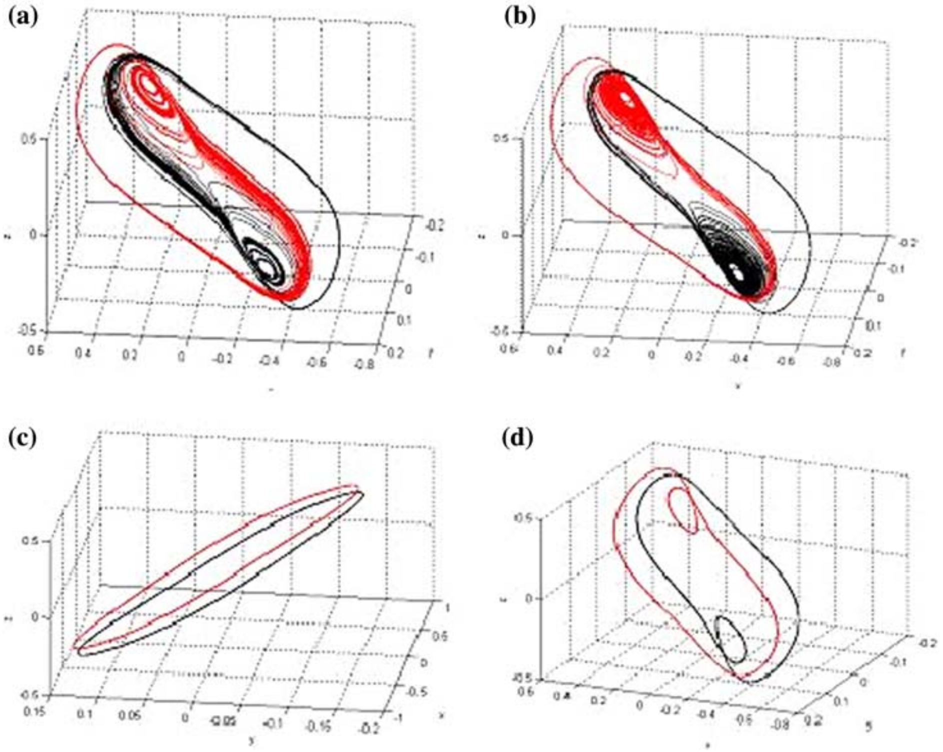

Figure 4. (a) and (b) Chaotic attractor appears if $q = \pm 0.0186$ and $q = \pm 0.02$; (c) and (d) limit cycles appears when $q = \pm 0.01$ and $q = \pm 0.015$.

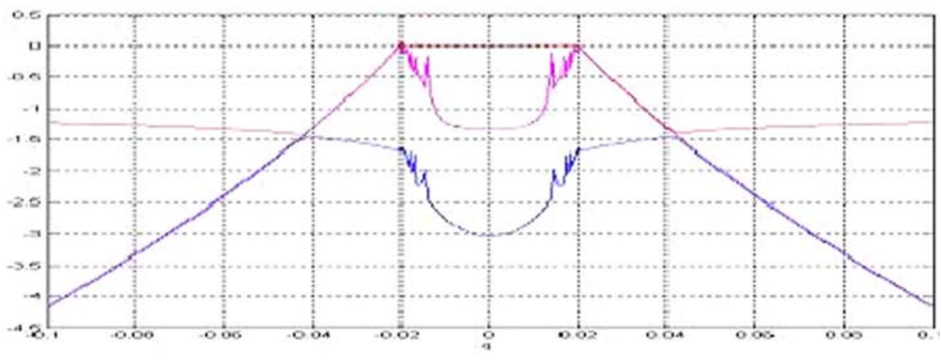

Figure 5. The Lyapunov exponents for parameter $-0.1 \leqslant q \leqslant 0.1$.

algorithms presented in [19,20]. This is conflict with the statement in [11] which asserted that the system is chaotic when $q = 0.0186$ without any details. The orbits of the system when $q = 0.0186$ are shown in figure 6. Due to the fact that LE computation is not always valid in studying complex dynamics of nonlinear

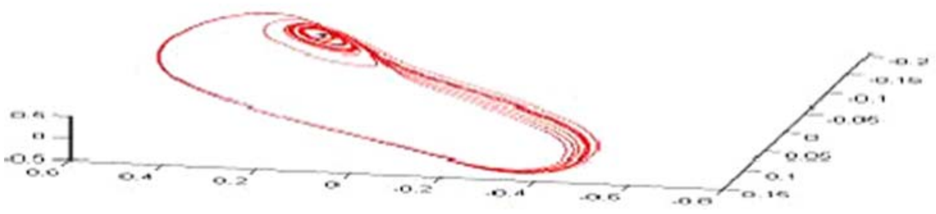

Figure 6. The Spiraling attractor of equation (1) with q=0.0186 and the equilibrium (0.2775, −0.1007, 0.2775).

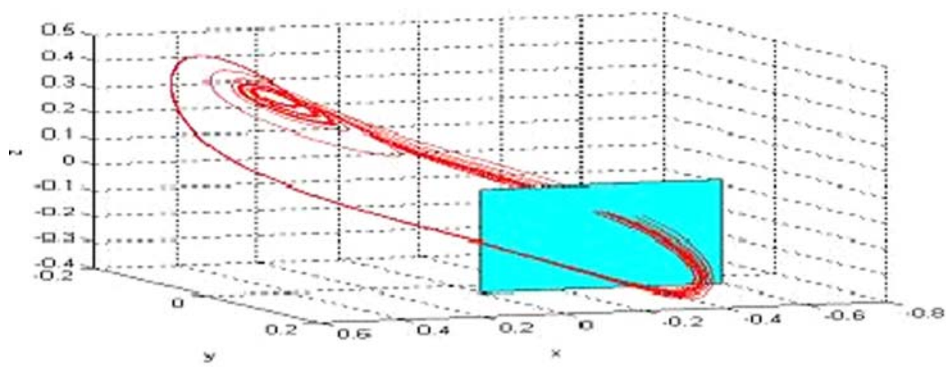

Figure 7. The attractor of (2) and cross-section M_2.

systems we study this system by virtue of a recent result of horseshoes theory in dynamical systems [12,13], we show that the system is chaotic by a rigorous computer-assisted proof.

7. Horseshoes in bromate-MA-ferroin system

In (2), let $\alpha = 18.7$, $\gamma = 4.35$, $\mu_1 = 0.44$, $\mu_2 = -1.43$, $q = 0.0186$, we have the attractor as shown in figure 7. Denote by $\varphi_1(x, t)$ the solution of (2) with initial condition x, i.e. $\varphi_1(x, 0) = x$. Consider the cross-section M_2 as shown in figure 7, with its four vertices being $(0, 0.05, 0)$, $(-0.6, 0.05, 0)$, $(-0.6, 0.05, -0.4)$ and $(0, 0.05, -0.4)$.

We will study the corresponding Poincaré map on a subset of M_2. We select the quadrangle $|ABCD|$ with its vertexes being $A(-0.3673, 0.05, -0.14117)$, $B(-0.3440, 0.05, -0.1369)$, $C(-0.3438, 0.05, -0.1384)$ and $D(-0.3666, 0.05, -0.1424)$.

$$P : |ABCD| \to M_2.$$

The map P is defined as follows: for each point $x \in |ABCD|$, $P(x)$ is the first return intersection point with M_2 under the flow with initial condition x.

Now we expect to find two subsets of $|ABCD|$ as the subset D_1, D_2 defined in Definition 1. By a great deal of computer simulation, we find two subsets a_1 and a_2 of $|ABCD|$. The four vertices of a_1 are $(-0.3673, 0.05, -0.14117)$, $(-0.36311, 0.05, -0.1404)$, $(-0.3625, 0.05, -0.14168)$ and $(-0.3666, 0.05, -0.1424)$.

The four vertices of a_2 are $(-0.36171,\ 0.05,\ -0.14015)$, $(-0.3440, 0.05, -0.1369)$, $(-0.3438, 0.05, -0.1384)$ and $(-0.36113, 0.05, -0.14144)$.

The subsets a_1 and a_2 of $|ABCD|$ are shown in figure 8(a) and (b).

As shown in figure 8, where l_1 and r_1 are the left side and right side of a_1, l_2 and r_2 are the left side and right side of a_2, respectively, Since $P(l_1)$ is located at the right of r_2, and $P(r_1)$ is located at the left side of l_1, it is easy to see that for every line γ connecting l_1 and r_1 in a_1, there exists a subline of $P(\gamma)$ which connects l_1 and r_2 in $|ABCD|$. Since $P(r_2)$ is located at the right of r_2, and $P(l_2)$ is located at the left side of l_1, it is easy to see that for every line $\bar{\gamma}$ connecting l_2 and r_2 in a_2, there exists a subline of $P(\bar{\gamma})$ which connects l_1 and r_2 in $|ABCD|$.

It is easy to see from figure 8 that every line l lying in $|ABCD|$ and connecting the side l_1 and r_2 has nonempty connections with a_1 and a_2. Furthermore, $P(l \cap a_1)$ connects l_1 and r_2 from the above arguments, $P(l \cap a_2)$ also connects l_1 and r_2. Therefore, it is easy to see, in view of Definition 1, that there exists a P-family with respect to these two subsets a_1 and a_2 for the map P. It follows from Theorem 2 that there exists an invariant set K of $|ABCD|$, such that P restricted to K is semi-conjugated to 2-shift dynamics. Let $h(P)$ be the entropy of the map P, it can be concluded from Lemma 3 that $h(P) \geqslant h(\sigma) = \log 2$, consequently the entropy of the map P is not less than log 2.

Numerical work shows that the average return time is 8.8114, the maximum return time is 9.6078, and the minimum return time is 7.8919. The topological entropy of the system is not less than $\log 2/8.8114 = 0.0787 > 0$ by Abramov's formula [14], thereby having a quantitative description of complex of dynamics.

In [11], it was asserted from the oscillation experiments that a continuously stirred tank reactor (CSTR) the BZ reaction could exhibit simple and complex periodic oscillations as well as chaotic behavior. Here, we have shown that the

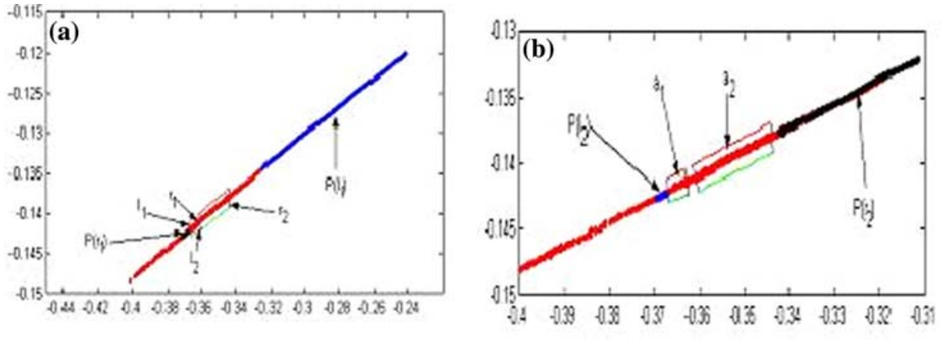

Figure 8. (a) The subset a_1, a_2 and the image of a_1; (b) The subset a_1, a_2 and the image of a_2.

attractors are chaotic by giving a rigorous verification for existence of horseshoes in the system. We have shown that the Poincaré map derived from the system is semi-conjugate to the 2-shift map, and the topological entropy of the system is not less than 0.0787.

It can be concluded from the symmetry as discussed in section 6 of system (1) that there exists horseshoes when $q = -0.0186$. In the same manner, we can discuss the system (1) with $q = \pm 0.02$.

8. Conclusion

Applying the concepts and techniques issued from dynamical systems theory, we have been able to show the existence of chaotic behavior in the bromate-MA-ferroin system. In this paper we present a rigorous computer-assisted proof for the existence of horseshoes in the bromate-MA-ferroin system. We show that the dynamics of the Poincaré map derived from the ordinary differential equations of the system is semi-conjugate to the 2-shift map, and the topological entropy of the system is not less than 0.0787. The proof is based on a newly established Theorem 2 from [12] on the existence of topological horseshoe and computer simulation.

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