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Effect of temperature and small amounts of metal ions on transient chaos in the batch Belousov–Zhabotinsky system

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Abstract

We report an effect of temperature and small amounts of metal ions on transient chaotic regime observed in the batch Belousov–Zhabotinsky oscillating chemical reaction catalyzed by ferroin. The transient chaos is quantified by values of the largest Lyapunov exponent and induction period. We have found that these values depend through the Arrhenius equation on the temperature if the initial ferroin concentration is varied in the range of $(0.87\text{--}3.5) \times 10^{-3}$ M. We show that inside this range transient chaos is characterized by linear response to injection of solutions containing metal ions, e.g., cerium(III), manganese(II), vanadyl(IV) or thallium(I). © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Chemical reactions may exhibit various dynamic regimes, for example, monotonic, regular and complex oscillations, chaos, etc. [1–4]. Complex oscillations and chaos have been usually observed in a continuously flow stirred tank reactor (CSTR) [1–6]. It has been also reported that transient chaotic oscillations are observed in the Belousov–Zhabotinsky (BZ) oscillating chemical reaction in a batch reactor [7–9]. Experimental and theoretical study of transient chaos in the BZ system indicates that transient chaotic regimes may be caused by a system slow motion along a horseshoe-type strange set [10,11]. These oscillations are associated with Z-shaped return maps [12]. Transient chaos may be described quantita-

tively by the average value of the largest Lyapunov exponent defined as [13]

$$\bar{\lambda}_L = \frac{1}{T} \int_{t_0}^{t_0+T} \lambda_L(t) dt, \quad (1)$$

where $\bar{\lambda}_L$ is the value of the largest Lyapunov exponent averaged over time, $\lambda_L(t)$ is the time-dependent value of the local Lyapunov exponent, T is the time interval of observation of the transient chaotic regime, and t_0 is the moment of time when transient chaos appears. We have shown that the Wolf algorithm [14] is applicable for the calculation of $\bar{\lambda}_L$ for sufficiently long transient chaotic time series [15]. For the sake of simplicity, in further text we will use notation λ_L for the value of $\bar{\lambda}_L$.

The BZ reaction exhibits various dynamic regimes depending on experimental conditions. Particularly, trace impurities in the malonic acid can substantially alter the dynamics and even the whole bifurcation structure of the BZ reaction [16,17]. The bifurcation structure of the BZ

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reaction also depends on the temperature [18]. Varying temperature in a narrow interval may induce bifurcations between various complex oscillations and chaotic regimes [19]. An increase of temperature may also induce a disappearance of regular oscillations through the Hopf bifurcation [20]. Experimental study of the BZ reaction indicates that the frequency of oscillations depends through the Arrhenius equation on the temperature [21–24].

An effect of trace amounts of chemical compounds on regular or chaotic oscillations observed in nonlinear chemical reactions has already found its application in analytical chemistry [25–30]. Particularly, regular oscillations in the BZ system have been used for the determination of trace amounts of metal ions because oscillation period depends linearly on the concentrations of these metal ions [25,26]. A procedure has been recently also reported to determine various chemical compounds using copper(II)-catalyzed oscillating chemical reaction between hydrogen peroxide and sodium thiocyanate in alkaline medium [27,28]. It has been also shown that trace amounts of manganese(II) or vanadium(IV) may be determined using transient chaos in the BZ system [29,30].

In the present Letter we report results of experimental studies of an effect of temperature and small amounts of metal ions on transient chaotic regime observed in the batch Belousov–Zhabotinsky oscillating chemical reaction catalyzed by ferroin. Studies are performed at various initial ferroin concentrations. The transient chaos is quantified by values of the largest Lyapunov exponent and induction period. We show that using these values one may also quantify a response of transient chaos either to temperature variations or to injection of solutions containing metal ions.

2. Experimental

All chemicals were of analytical grade. Doubly distilled water was used for solutions preparation. Studies were conducted in a 100 ml reactor at a stirring rate of 800 rpm. The volume of reaction mixture was 40 ml. The reactor was thermostated with exact ± 0.1 grade. Temperature was varied in

the range 12–35°C. The metal ions' effect on transient chaos was studied by injection of their aqueous solution (0.5 mL) into 39.5 ml of the BZ reaction mixture after 30 s of its preparation. The mixing solutions were chosen so that the final solution is characterized by following concentrations of reagents: $[\text{KBrO}_3]_0 = 0.115$ M; $[\text{H}_2\text{SO}_4]_0 = 0.32$ M; $[\text{MA}]_0 = 0.68$ M. The initial ferroin concentration (C_{Fe}) was varied in the range $(0.87\text{--}3.5) \times 10^{-3}$ M. The concentration of metal ions was varied in the range $10^{-4}\text{--}10^{-12}$ M. The concentrations of KBrO_3 , H_2SO_4 and malonic acid were kept fixed in all experiments. The state of the system was monitored by measuring the potential of a platinum electrode using a silver–silver chloride electrode as a reference. The impedance-matched electrode signals were fed via a Data Translation A/D converter board into a personal computer. Signals were recorded as a function of time with time step 0.1 s.

3. Results and discussion

A time dependence of the Pt-electrode potential is presented in Fig. 1a. The long-lived relaxation oscillations appear in the system after the induction period (T_i). They consist of a large-amplitude oscillation followed by one small-amplitude oscillation shown in Fig. 1a. Contrary to the periodic oscillations, amplitudes of large-amplitude oscillations and time intervals between their maxima are not constant. These oscillations are not periodic but chaotic [8,15,29,30]. Fig. 1b gives the projection of the phase portrait on the plane reconstructed from the time series of Pt-electrode potential by time-delay technique [31].

The phase portrait presented in Fig. 1b corresponds to a transient motion of the system along the horseshoe-type strange set. It has been shown recently that the BZ reaction catalyzed by ferroin exhibits a variety of transient complex regimes in the same concentration range as reported here [8,15]. These transients are caused by slow decrease of concentrations of bromate and malonic acid in the course of the reaction. If these concentrations are fixed, e.g. if experiments are conducted in a CSTR, then the system exhibits various

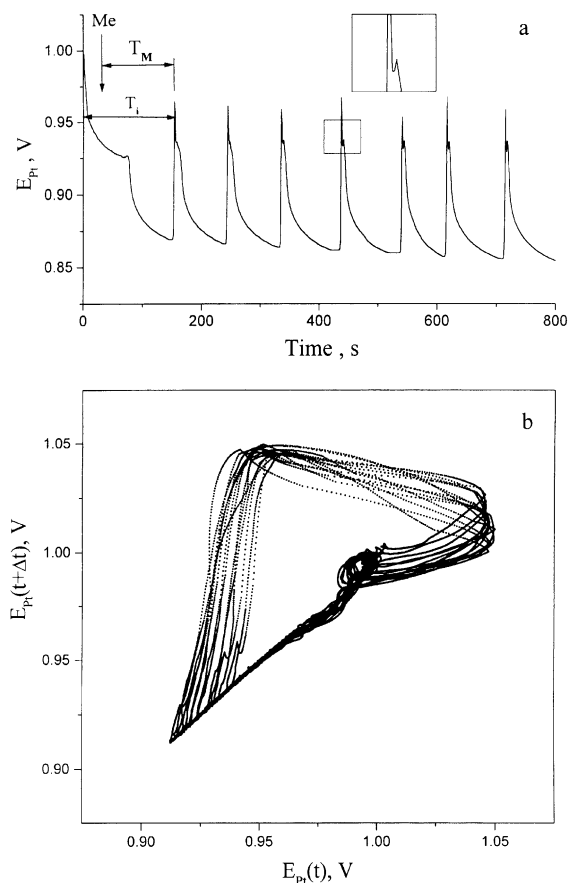


Fig. 1. Time series (a) and corresponding phase portrait (b) illustrating transient regime observed in a batch at the following initial concentrations of reagents: $[\text{KBrO}_3]_0 = 0.115$ M; $[\text{H}_2\text{SO}_4]_0 = 0.32$ M; $[\text{MA}]_0 = 0.68$ M; $C_{\text{Fe}} = 1.7 \times 10^{-3}$ M. Phase portrait has been reconstructed using $\Delta t = 1$ s.

mixed-mode oscillations and chaotic behavior. Even the simplest mixed-mode regime, L^1S^1 (one large amplitude loop followed by a single small amplitude loop), appears as rotations on the slow manifold given by a horseshoe-type strange set [10]. Therefore, slow decrease of the concentrations of bromate and malonic acid in batch corresponds to an unpredictable trajectory on the slow manifold. It results in the appearance of an aperiodic trajectory, presented in Fig. 1. The aperiodicity may be caused either by transient chaotic behavior [3] or by experimental noise reflecting the sensitivity of system to external perturbations [13]. In both cases a sensitivity of system to external

perturbations may be characterized by the largest Lyapunov exponent given by Eq. (1).

Our experiments show that the transient chaotic regime does not change qualitatively in the range of $C_{\text{Fe}} = (0.87\text{--}3.5) \times 10^{-3}$ M. In this range of C_{Fe} one may attribute the transient chaotic regime by the value of the largest Lyapunov exponent given by Eq. (1). Fig. 2a illustrates that λ_L decreases with an increase of C_{Fe} . Another quantitative characteristic of the transient chaotic regime, the induction period, also depends on C_{Fe} as shown in Fig. 2b. Contrary to λ_L , the value of T_i increases with an increase of C_{Fe} .

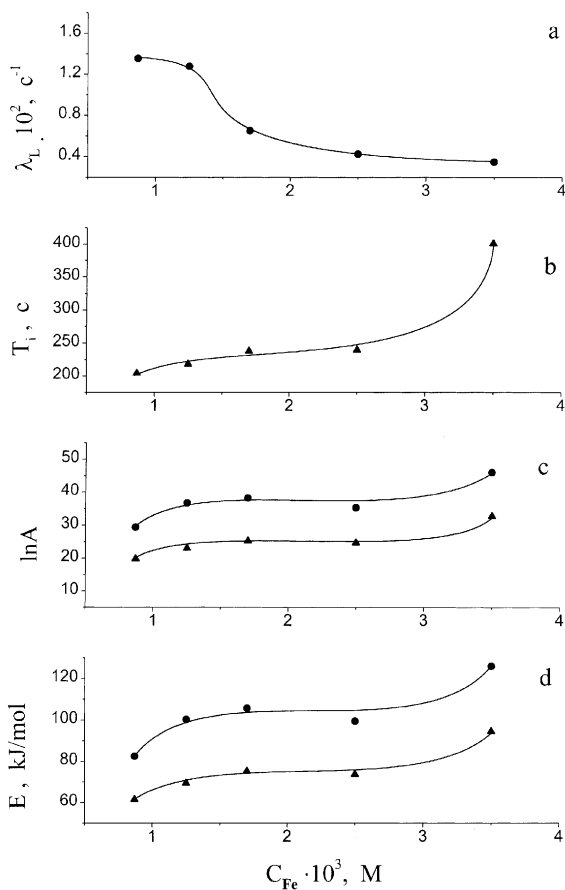


Fig. 2. Dependence of λ_L (a), T_i (b), preexponential factors (c), and effective activation energies (d) on initial ferroin concentration. In panels (c) and (d) filled dots correspond to parameters for Eq. (2) and filled triangles correspond to parameters for Eq. (3).

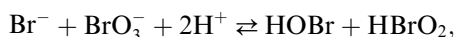
We have found that values of induction periods and the largest Lyapunov exponents depend through the Arrhenius equation on the temperature in the range of $C_{\text{Fe}} = (0.87\text{--}3.5) \times 10^{-3}$ M:

$$\lambda_L = A_\lambda \exp(-E_\lambda/RT), \quad (2)$$

$$1/T_i = A_i \exp(-E_i/RT), \quad (3)$$

where both λ_L and $1/T_i$ have dimension of inverse time, as is usual for Arrhenius-like dependencies. In Eqs. (2) and (3) E_λ and E_i give the values of effective activation energies for the largest Lyapunov exponent and the inverse value of the induction period, and the values of A_λ and A_i give the corresponding preexponential factors. The correlation coefficients for the Arrhenius equations were more than 96% in all cases. Effective activation energies and preexponential factors depend on the initial ferroin concentration as illustrated by Fig. 2c,d. An increase of C_{Fe} slightly increases them. However, in the range of $C_{\text{Fe}} = (1.2\text{--}2.5) \times 10^{-3}$ M the values of effective activation energies and preexponential factors are almost constant.

The BZ reaction is a complex chemical process which is characterized by more than 80 elemental chemical reactions [32]. Therefore, values of λ_L and T_i are complex functions of rate constants of these reactions as well as initial concentrations of reagents. As a result, effective activation energies for λ_L and T_i are complex unknown functions of the activation energies of elemental chemical steps. However, some conclusions may be drawn from a comparison of the obtained results with activation energies for some of the elemental steps as well as with effective activation energies for frequency of regular oscillations. It has been reported that temperature dependence of frequency of regular oscillations is characterized by effective activation energies in the range of 62–82 kJ/mol and their values do not depend significantly on the catalyst (cerium(III) or manganese(II)) or substrate used in the BZ system [21–24,33–35]. This allowed one to conclude that the activation energy that characterizes temperature dependence of the oscillation frequency is associated with the following reaction [35]:



$$E_a = 54 \text{ kJ/mol}$$

The values of activation energies reported in this Letter are in the range of 60–95 kJ/mol for T_i and in the range of 80–125 kJ/mol for λ_L , which is higher compared to activation energies of regular oscillations. Moreover, the data shown in Fig. 2 indicate a tendency of an increase of both activation energies with increasing C_{Fe} . Both these observations may indicate that effective activation energies for λ_L and T_i are associated not only with the described chemical reaction, but also with reaction between ferroin and organic species, such as bromomalonic acid or bromotartronic acid.

The data presented in Fig. 2 illustrate the effect of temperature and initial ferroin concentration on the transient chaos in the BZ reaction. Impurities of reagents or small amounts of various chemical compounds is another factor that may affect the transient chaotic behavior. Particularly, it has been shown that a sensitivity of transient chaotic regime in the BZ reaction may be used for the determination of pico amounts of manganese(II) [29]. For the determination one should calculate the largest Lyapunov exponent and the characteristic time interval (T_M). The value of T_M is different from T_i . It is defined as the time interval between the injection of a solution containing chemical compound into the system and the first maximum of the Pt-electrode potential as illustrated in Fig. 1a. Experiments have shown that there exists a linear dependence between the product $\lambda_L T_M$ and the logarithm of manganese(II) concentration [29]. Using these results, we have performed a study of the effect of cerium(III), vanadyl(IV) and thallium(I) ions on the transient chaos.

Fig. 3 gives typical dependencies of $\lambda_L T_M$ on $\lg C_{\text{Me}}$ for these metal ions as well as for manganese(II). In general, dependence of $\lambda_L T_M$ on metal ion concentration is a complex function. Particularly, this dependence is nonmonotonic for cerium(III). It has a deep minimum at 10^{-7} M of cerium(III). This value of metal ion concentration we denote as C_L . At cerium(III) concentrations above C_L the product $\lambda_L T_M$ depends linearly on the logarithm of metal ion concentration, whereas at cerium(III) concentrations below C_L this dependence is characterized by nonmonotonic behavior and tremendous scatter of points. Scattering of points below $C_L = 10^{-9}$ M is less for vanadyl(IV)

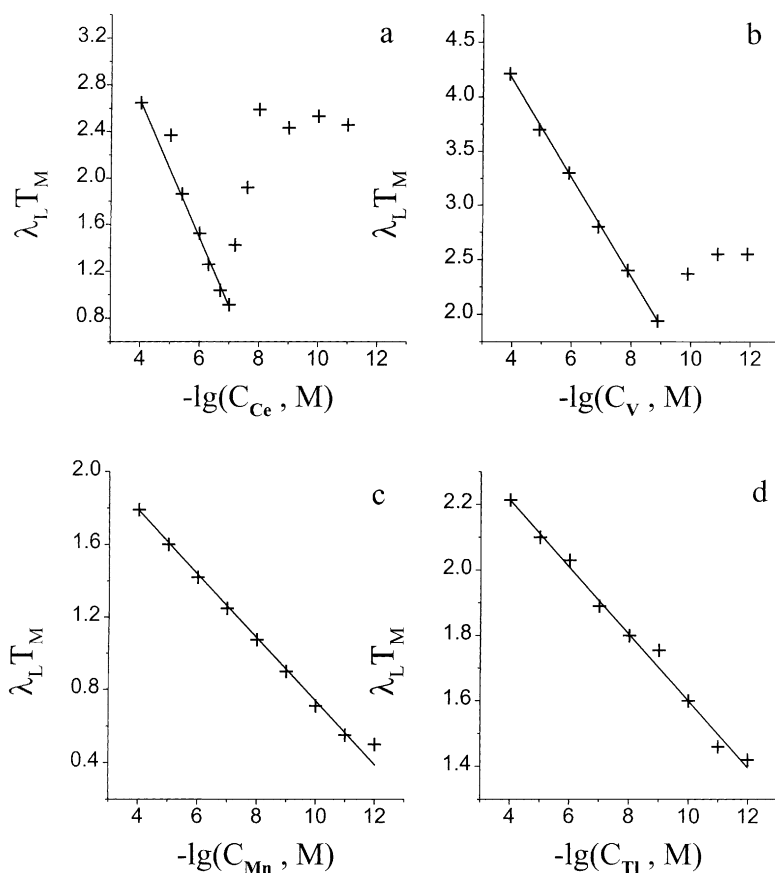


Fig. 3. Dependence of $\lambda_L T_M$ on the metal ion concentration: (a) for cerium(III) at $C_{Fe} = 1.7 \times 10^{-3} M$; (b) for vanadyl(IV) at $C_{Fe} = 1.7 \times 10^{-3} M$; (c) for manganese(II) at $C_{Fe} = 1.7 \times 10^{-3} M$; (d) for thallium(I) at $C_{Fe} = 1.7 \times 10^{-3} M$.

as shown in Fig. 3b. However, above C_L the dependence of $\lambda_L T_M$ on the logarithm of vanadyl(IV) concentration is also linear. Linearity of dependence of $\lambda_L T_M$ on $\lg C_{Me}$ is more pronounced for manganese(II) and thallium(I) in the whole range of concentrations studied as follows from the data presented in Fig. 3c,d. Therefore, analysis of data presented in Fig. 3 allows one to approximate dependence of $\lambda_L T_M$ on $\lg C_{Me}$ by a straight line in a certain concentration range of metal ions:

$$\lambda_L T_M = \alpha - \beta \lg C_{Me}, \quad (4)$$

where C_{Me} is the concentration of metal ions.

Eq. (4) illustrates that transient chaos is characterized by a linear response to injection of metal ions. The parameter β may be considered as sensitivity of transient chaos to given metal ions. The

lower boundary of the concentration range defines the value of C_L below which Eq. (4) does not describe the system response, i.e. transient chaos does not exhibit linear response to injection of solutions containing metal ions.

Table 1 indicates that β and C_L depend on C_{Fe} as well on the nature of metal ions. However, the sensitivity of transient chaos defined by the value of β always decreases with an increase of C_{Fe} . From the data presented in Fig. 2a it follows that the largest Lyapunov exponent decreases if C_{Fe} increases. Therefore, the sensitivity of linear response of transient chaos to injection of small amounts of metal ions decreases with a decrease of the largest Lyapunov exponent obtained for unperturbed transient regime. This result illustrates that the largest Lyapunov exponent defines a

Table 1

Values of β and C_L that characterize linear response of transient chaos to injection of solutions containing cerium(III), manganese(II), vanadyl(IV) or thallium(I) ions at various initial ferroin concentrations

[ferroin] ₀ × 10 ³ (M)	Ce ³⁺		Mn ²⁺		VO ²⁺		Tl ⁺	
	β	$-\lg(C_L, \text{M})$	β	$-\lg(C_L, \text{M})$	β	$-\lg(C_L, \text{M})$	β	$-\lg(C_L, \text{M})$
0.87	0.73	7	0.58	7	0.42	9	0	–
1.3	0.036	12	0.28	12	0.42	12	0.1	12
1.7	0.032	12	0.17	12	0.43	12	0.075	10
2.5	0	–	0.17	9	0.25	9	0	–
3.5	0	–	0.18	8	0.09	8	0	–

sensitivity of chaotic regime to injection of solutions containing metal ions.

The data presented in Table 1 also indicate that at $C_{\text{Fe}} = 1.3 \times 10^{-3} \text{ M}$ and $C_{\text{Fe}} = 1.7 \times 10^{-3} \text{ M}$ the linear response of transient chaos holds in the widest range of metal ion concentrations injected into the system. At these two values of C_{Fe} the value of C_L equals 10^{-12} M for all metal ions with one exception for thallium at $C_{\text{Fe}} = 1.7 \times 10^{-3} \text{ M}$. Therefore, the range of metal ion concentrations where transient chaos exhibits linear response to injection of metal ions does not depend significantly on the nature of metal ions.

Comparison of temperature effect and effect of metal ions injection on transient chaos indicates appearance of a connection between these two effects. In the range of $C_{\text{Fe}} = (1.2\text{--}2.5) \times 10^{-3} \text{ M}$ the values of effective activation energies and pre-exponential factors are almost constant. Namely, inside this range of C_{Fe} the transient chaos exhibits sensitivity to metal ion injection in the widest range of their concentrations.

4. Conclusions

Our studies have shown a possibility to quantify a response of transient chaotic regimes to various perturbations by using values of the largest Lyapunov exponents and induction periods. We illustrate that both these values depend through the Arrhenius equation on temperature. The effect of metal ion injection on transient chaos is described by Eq. (4) in a certain range of concentrations of these metal ions. We have found that transient chaos exhibits a sensitivity to very low concentrations of metal ions, down to 10^{-12} M .

This shows possibility for further progress in the application of chemical chaos to analytical chemistry. Moreover, the study reported here highlights the most effective way of searching for an appropriate chaotic regime that may be used for quantitative determination of pico amounts of various chemical compounds. On one hand, the value of λ_L should be as large as possible. On the other hand, the optimal conditions for determination may be found inside a range for control parameter where parameters for temperature dependence of λ_L and T_i do not depend significantly on the control parameter. Particularly, the results presented in Fig. 3 and in Table 1 indicate a possibility for the development of a highly sensitive method for thallium(I) determination in water solutions with a detection limit of 10^{-12} M . Dependence between $\lambda_L T_i$ and the logarithm of thallium(I) concentration gives a calibration plot for thallium(I) determination because each value of $\lambda_L T_i$ corresponds to a single value of thallium(I) concentration, contrary to cerium(III) and vanadyl(IV).

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