Period-Adding Bifurcations in Mixed-Mode Oscillations in the Belousov−Zhabotinsky Reaction at Various Residence Times in a CSTR

Malgorzata Rachwalska

Department of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Cracow, Poland

Andrzej L. Kawczyński*

Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

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Periodic patterns of mixed-mode oscillations with successive numbers of small-amplitude oscillations followed by one large-amplitude oscillation (period-adding phenomenon) have been observed in the asymptotic regime of the Belousov−Zhabotinsky reaction (bromate−malonic acid−ferroin) in a CSTR (continuously stirred tank reactor) at decreasing residence times. Such period adding has been predicted by a simple model proposed recently for a qualitative description of asymptotic and transient oscillations observed in the BZ system. Patterns qualitatively corresponding to the experimental ones are obtained in this model.

Introduction

Various mixed-mode periodic as well as chaotic oscillations have been observed experimentally in continuously stirred tank reactors (CSTRs) in asymptotic regimes. Most experiments have been performed with the Belosov−Zhabotinsky reaction (BZ),[1−6] but mixed-mode oscillations (MMO) have been found also in other chemical systems.[2−4,7,8] MMO exhibit patterns of the type LS_n, where L denotes an oscillation with large amplitude, S means an oscillation with substantially smaller amplitude as compared with L, and $n = 0, 1, 2, ...$. In these patterns S oscillations have their minima close to maximal values of L amplitudes or (but not and) they have their maxima close to minimal values of L. Recently, new type of asymptotic mixed-mode oscillations LS_ns_m have been observed in the BZ reaction with ferroin as the catalyst,[9] i.e., sustained periodic oscillations in which small-amplitude oscillations have their minima at a maximal value of L and, in the same pattern, other small amplitude oscillations have maxima close to the minimal value of L.

It is rare in experiments to start just from initial conditions belonging to a periodic or strange attractor. Therefore, transient regimes are usually observed before dynamical systems approach their attractors. One may distinguish two types of transient regimes in dissipative, dynamical systems. One of them may be called the Lyapunov neighborhood of an attractor, if a transient trajectory of the system approaches exponentially the attractor. This neighborhood is so close to the asymptotic trajectory that a linear approximation for the difference between the transient trajectory and the attractor is valid. Therefore, in the Lyapunov region the transient oscillations have the same patterns as the asymptotic ones and only quantitative differences between the both patterns can be observed. Outside of the Lyapunov neighborhood qualitative differences between transient and asymptotic patterns may appear. For example, regular sequences of transient MMO in CSTR at low flow rates of the reagents have been found in the BZ system (malonic acid (MA), $KBrO_3$, H_2SO_4, and ferroin).[10] Asymptotic, simple periodic (L) oscillations for long residence time ($\tau = 66.7$ min) were preceded by transient MMO with patterns varying from $(LS_3)2(LS_2)6(LS_1)$ to $(LS_5)(LS_3)2(LS_2)3(LS_1)$, if inflow ferroin concentration was changed from 0.75×10^{-3} to 3.13×10^{-3} M, whereas inflow concentrations of remaining reactants were kept constant. The appearance of these transient regular MMO followed by asymptotic simple periodic oscillations (L) demonstrates that in initial period of time the system is out of the Lyapunov neighborhood. Similar behavior with the "transient period adding" has been found in the BZ system;[11] i.e., transient patterns LS_i with $i = 1, 2, ..., 7$, followed by L oscillations only, were observed in turn, if inflow concentration of MA was changed from 0.109 to 0.163 M.

There appears the natural question concerning dynamical systems in general: *does a subpattern, observed in a transient regime at some value of a control parameter, appear as an asymptotic one for appropriately changed value of the parameter?* There are no obvious reasons indicating that this question cannot have the positive answer. For the BZ system this question reads as follows: *can a subpattern observed in transient regime at some value of the residence time appear as an asymptotic one, if the residence time is decreased?* To our best knowledge there is a common believe that the answer for the above questions is positive, but this problem has not been studied in detail. In the case of the positive answer the next, natural question appears: *which of observed transient subpatterns does appear in an asymptotic regime, if the residence time is progressively decreased?*

The aim of this paper is to study these questions in more details. Experiments in CSTR with the BZ reaction (MA, $KBrO_3$, H_2SO_4 and $Fe(phen)_3^{2+}$) in CSTR have been performed for various residence times for one of the values of initial concentrations of the reactants studied previously.[10] Both transient as well as asymptotic patterns have been investigated. Moreover, we show that qualitatively identical transient and asymptotic patterns are obtained in the simplest dynamical model proposed recently[9,10,12] for the qualitative description of

* Corresponding author. E-mail:alk@ichf.edu.pl.

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regularities in transient and asymptotic MMO observed experimentally in the BZ reaction. Studies of this model show that the most important phenomenon which appears with changes of a bifurcation parameter is the period-adding sequence of bifurcations.[13,14] These results have been prompted us to look for the period adding in the experiments.

Experimental Results

The experimental setup used in the present measurements is similar to that described previously.[9,10] All experiments were carried out in a CSTR at a temperature of 21 °C. The total volume of the reaction mixture was 40 cm^3, and the stirring rate was 900 rpm. In all experiments the initial concentrations of the reactants in the CSTR were identical and equal to the following: $[KBrO_3] = 0.19$ M; $[MA] = 0.68$ M; $[H_2SO_4] = 0.32$ M; $[Fe(phen)_3^{2+}] = 0.001\,125$ M. A period of time from the moment of mixing of the reactants until the registration of the first LS_i sequence was about 2 min. Various values of inflows of the reactants were used which allowed for the change of the residence time τ from about 30 to about 2 min. The measurements have been performed at least to 8 residence times in order to be capable to observe asymptotic regular MMO oscillations with not very long periods.

An example of time series observed in experiments is shown in Figure 1. This time series was obtained for the residence time equal to 6 min, and it is described by the pattern $(LS_6)(LS_5)2(LS_4)n(LS_3)$. The transient regime appears as sequences of large amplitude (L) oscillations followed by a decreasing number of small amplitude (S) oscillations, and then the system exhibits sustained LS_3 oscillations. One asymptotic pattern LS_3 is shown only, but this pattern repeats many times up to the end of the experiment.

Other examples of time series are presented in Table 1. The patterns shown in Table 1 are reproducible in the sense that they repeat at least in the subsequent two experiments. The decreasing of the residence time causes that in the transient patterns more small amplitude oscillations appear in their subpatterns. It is noteworthy that the decreasing of τ causes the increase by one of a number of small amplitude oscillations in the asymptotic patterns from LS_1 to LS_5. This sequence of the patterns is consistent with five initial patterns observed in the period-adding phenomenon.[15,16]

At some values of τ we have not found periodical patterns although we continued the measurements up to 12 residence times. The irregular mixture of L and LS_1 has been observed at $\tau = 16$ min. The other irregular mixture of subpatterns LS_7 and LS_8 has been observed at $\tau = 3.9$ min in a long period of time up to 12 τ. Also at $\tau = 2.4$ min a irregular pattern consisting of subpatterns with L followed by dozen of S oscillations has been observed. It is noteworthy that the irregular mixture of L and LS_1 appears at the value of τ belonging to the interval between two values for which the asymptotic patterns L (for $\tau = 21$ min) and LS_1 (for $\tau = 12.8$ min) have been observed. It is not excluded that the two other irregular patterns also appear in intervals between subsequent periodical patterns, but we are not able to solve this problem in our experimental setup. At the moment we are not able to explain if the observed irregular patterns are determined by deterministic chaotic dynamics or they are caused by drifts in the inflows of the reactant in our peristaltic pumps which induces the switching of the system between two subsequent MMO patterns.

Model

The simple three-variable model which qualitatively describes various asymptotic MMO observed in the BZ reaction has been studied recently.[13,14] This model was also helpful in the successful searches of new types of MMO with patterns LS_nS_m.[9] Detailed studies of this model reveal a rich variety of bifurcation sequences such as period doubling, period adding, broken Farey

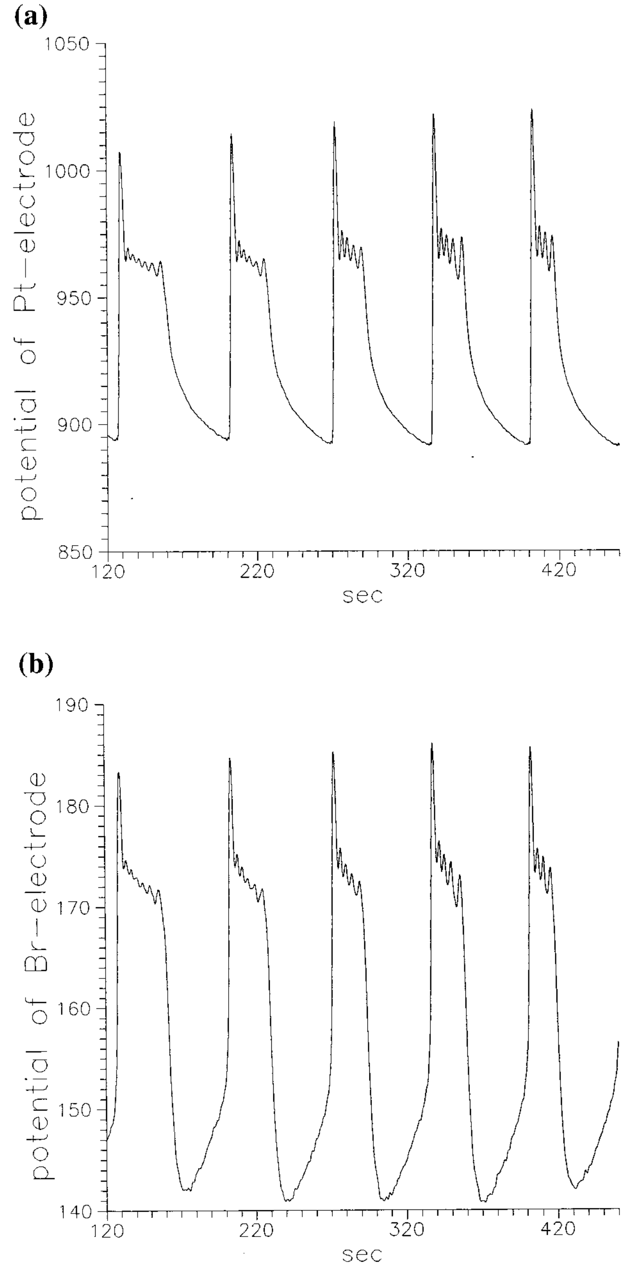

Figure 1. Time oscillations of potential Pt (a) and Br (b) electrodes for the CSTR experiment at the residence time $\tau = 6$ min. The pattern $(LS_6)(LS_5)2(LS_4)n(LS_3)$ is observed. One of subpatterns LS_3 observed in the asymptotic regime is shown only.

TABLE 1: Transient and Asymptotic Patterns Observed in the BZ Reaction in CSTR for Various Residence Times (τ) at the Conditions $[KBrO_3] = 0.19$ M, $[MA] = 0.68$ M, $[H_2SO_4] = 0.32$ M, $[Fe(phen)_3^{2+}] = 1.125 \times 10^{-3}$ M, and $T = 21$ °C and Values of the Parameters Determining the Dynamics of $q(t)$ in the Four-Variable Model

τ, min	pattern	q_1	g	$q(0)$
27.2	$(LS_4)(LS_3)3(LS_2)8(LS_1)n(L)$	0.37	0.0013	0.225
12.8	$(LS_5)2(LS_3)5(LS_2)n(LS_1)$	0.2695	0.0049	0.222
8.0	$(LS_5)(LS_4)3(LS_3)n(LS_2)$	0.255	0.0053	0.2215
6.0	$(LS_6)(LS_5)2(LS_4)n(LS_3)$	0.242	0.0055	0.219
5.1	$(LS_7)(LS_5)(LS_6)n(LS_4)$			
4.8	$(LS_8)n(LS_5)$	0.226	0.0280	0.200

trees, and more complex bifurcations.[13,14,16] The simple extension of this model by addition of the fourth variable allowed us to model regularities in transient patterns as well as asymptotic ones observed experimentally in the BZ reaction.[10-12] The three-variable version of the model has the form

$$\dot{v} = r[u - (v - v_1)(v - v_2)(v - v_3) - a] = rf(u, v) \quad (1)$$

$$\dot{u} = b - b_1 p - b_2 v - u = g(u, v) \quad (2)$$

$$\dot{p} = q(v - p) \quad (3)$$

Assume that the parameters in eqs 1−3 are kept constant and have the values $v_1 = 10$, $v_2 = 11$, $v_3 = 20$, $a = 150$, $b = 436.6$, $b_1 = 3.714$, $b_2 = 21.7$, and $q = 0.23$, whereas r is the bifurcation parameter, which mimics the changes of the residence time τ in the experiments. The asymptotic patterns presented in Table 1 may be obtained for the following values of the bifurcation parameter: LS_1 for $r = 0.07$; LS_2 for $r = 0.067$; LS_3 for $r = 0.066$; LS_4 for $r = 0.065$; LS_5 for $r = 0.06457$. All these patterns exist in some intervals of all parameters. The appearance of succeeding patterns is scaled according to the formula[17]

$$r_n - r_\infty = \text{constant} \times \frac{1}{n^2} \quad (4)$$

where r_n denotes the value for which the pattern LS_n appears and r_∞ is the value of r at which the period-adding sequence is finished, which means that infinite number of S oscillations appear in the asymptotic pattern LS_∞.

To model transient patterns together with asymptotic ones the four-variable model must be used, in which the parameter q is replaced by the additional variable denoted by the same symbol. The additional variable is necessary to mimic an accumulation of the bromomalonic acid, which is the very important intermediate product in the BZ reaction.[18] Thus, the model consists of eqs 1−3 and the following equation which describes an evolution of the variable q:

$$\dot{q} = -\gamma(q - q_1) \quad (5)$$

Let us note that dynamics for the variable $q(t)$ is as simple as possible and does not depend on other variables. It depends only on an initial value of $q(0)$ and two parameters: γ which determines the exponential growth of q and q_1 which defines the asymptotic value of q. It is noteworthy that both models are structurally stable. This means that small changes in the right-hand sides of eqs 1−3 and 5 do not cause qualitative changes in the asymptotic patterns (trajectories). For all other parameters constant, a value of $q(0)$ determines the number of S oscillations in the first subpattern LS_i of a transient regime. The decrease of $q(0)$ leads to the increase in a number of S oscillations in LS_i. A value of q_1 determines a number of S in an asymptotic regime. The decrease of q_1 causes the increase of a number of S in the asymptotic pattern. The number of subpatterns which appear in the transient regime is controlled by γ and the difference between q_1 and $q(0)$. Decreasing of γ or increasing of $q_1 - q(0)$ one can obtain transient patterns with a greater number of subpatterns LS_i. Let us notice that for infinite time the four-variable model reduces to the three-variable one described by eqs 1−3 with $q = q_1$. The values of the parameters q_1 and γ and the initial values of $q(0) = q_0$ which give patterns in transient and asymptotic regimes qualitatively identical to experimental ones are given in Table 1. For these patterns the value of r is equal to 0.065, and all other parameters in eqs 1−3 are equal to values given above. In this case we

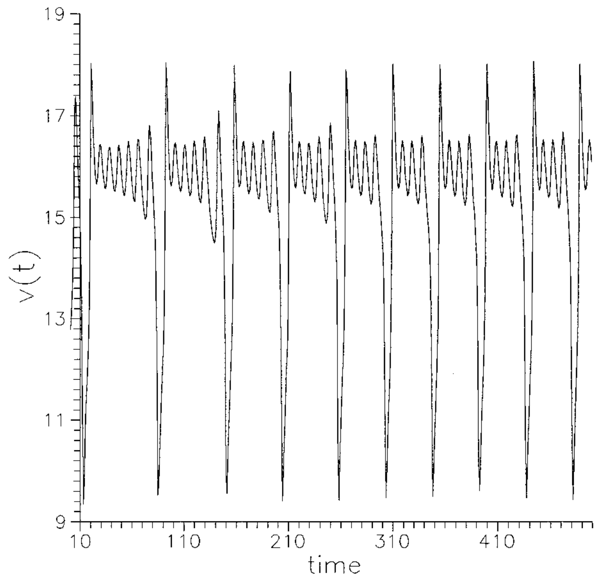

Figure 2. Time oscillations of the variable $v(t)$ for the model (1)−(4). The parameters in eqs 1−3 are the following: $v_1 = 10$; $v_2 = 11$; $v_3 = 20$; $a = 150$; $b = 436.6$; $b_1 = 3.714$; $b_2 = 21.7$; $q = 0.23$; $r = 0.066$; $q_1 = 0.242$; $\gamma = 0.0055$; $q_0 = 0.219$. The pattern $(LS_6)(LS_5)2$-$(LS_4)n(LS_3)$ similar to that in Figure 1 is shown. One of subpatterns LS_3 observed in the asymptotic regime is shown only.

obtain almost complete correspondence between the experimental results shown in Table 1 and the model. It is only the pattern $(LS_7)(LS_5)(LS_6)n(LS_4)$ that we cannot reproduce with the dynamics of q assumed in the model, but it can be reproduced if a dynamics for $q(t)$ richer than its exponential growth is used. Of course, identical sequences of patterns may be also obtained for other selections of values of all parameters.

Conclusions

Our experimental results show that *if a transient subpattern is observed in the BZ system at some value of the residence time, then it appears as an asymptotic one at smaller values of the residence time.* In this case the answer to the question mentioned in the Introduction seems to be positive. Moreover, from our experiments follow that *the last subpattern observed in the sequence of transient subpatterns appears in turn in all but one of asymptotic regimes, if the residence time is progressively decreased.* One exception is the pattern $(LS_7)(LS_5)$-$(LS_6)n(LS_4)$, in which the monotonic decrease of the number of S in subsequent subpatterns is not satisfied (LS_5 is followed by LS_6). Let us mention that this pattern cannot be so easily reproduced as all the remaining ones.

However, the results described in the paper of ref 11 in which inflow concentrations of reactants were far removed from those studied in the paper of ref 10 seem to show that the answer for the second question asked in the Introduction may be negative. Namely, the monotonic increase of the number S oscillations in the first subpatterns of the patterns was observed with decrease of the residence time in some range of inflow concentration of MA (transient period adding), but asymptotic regimes consisted of L oscillations. These experimental results were reproduced by the model (1)−(4), of course, with values of the parameters different from those used in this paper. It is not excluded that experiments with inflow concentrations of the reactants the same as used in ref 11 but with shorter residence times may allow for observations that are consistent with the positive answer for the first question.

Detailed studies of the three-variable model (eqs 1−3) reveal a rich variety of bifurcation sequences such as period doubling, period adding, broken Farey trees, and more complex bifurcations.[13,14] These studies may be helpful in experimental searches not only for a particular MMO with a given pattern but also for sequences of bifurcations. In this paper the initial sequence of period-adding bifurcations for the asymptotic regime has been found. Our experimental setup allowed us to change the residence time by rather large steps, and therefore, we are not able to observe asymptotic periodic patterns (LS_n) with $n > 6$. The irregular mixtures of subpatterns such as L and LS_1 or LS_7 and LS_8 have been observed in asymptotic regimes at values of the residence times between those corresponding to regular asymptotic patterns. These observations suggest that the period-adding sequence seems to appear according to the discussed model. Pure period adding that is the appearance of patterns LS_1, LS_2, ... LS_n with only chaotic orbits between them or with direct transformation of the one of these periodic to the next one, as it was observed in the other system,[15,16] seems to be excluded.

The model given by eqs 1−4 is capable to reproduce in a qualitative manner almost all experimental observations, although it does not have a simple relation to any realistic kinetic scheme of the BZ reaction. However, the model is very simple and describes also regularities in complex transient regimes reported previously.[10,11] Moreover, some qualitative correspondence between the variables of the model and the most important reagents of the BZ reaction may be suggested. The dynamics of variable v mimics an autocatalytic reagent, and therefore, it may correspond to [$HBrO_2$]. The variable u is involved in a "negative feedback" and may be related to [Br^-]. The variable p can be associated with the catalyst concentration. The additional variable q may mimic an accumulation of the bromomalonic acid (BMA) in the BZ reaction. It is reasonable to assume that the decrease of the residence time causes a decreasing of an asymptotic concentration of BMA, because reactants which produce BMA contact themselves shorter in the CSTR. Asymptotic concentrations of BMA are described by q_1, which should decrease with decreasing τ. Richer asymptotic patterns have been observed with decreasing τ in experiments as it was mentioned above, and a similar dependence has been found in the model (see Table 1). Moreover, it seems reasonable to assume that the decrease of τ shortens the achievement of the asymptotic regime for the concentration of BMA. This assumption should correspond to the increase of γ in the model. The values of γ given in Table 1 confirm this assumption. The decreasing values of $q(0)$ for decreasing τ given in Table 1 are selected as such to ensure the agreement between the model and the experiments. It is noteworthy that we were able to reproduce almost all patterns observed in the experiments. Such correspondence has been not always achieved for more realistic chemical models.

It is noteworthy that our simplest model not only can describe qualitatively known experimental results but is also useful in predictions of new regimes in experiments with nonlinear dynamical systems.

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